U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-270 220

A First Order Mass Balance Model for the Sources, Distribution and Fate of PCBs in the Environment

Versar, Inc, Springfield, Va

Prepared for

Environmental Protection Agency, Washington, D C

27 Jul 77

PB 270 220

EPA 560/6-77-008

A First Order Mass Balance Model for the Sources, Distribution and Fate of PCBs in the Environment

JULY 1977

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C., 20460

DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA 560/6-77-006	2.	3. Recipient's Accession No.
4. Title and Subtitle: A First Order Mass Balance Model for the Sources, Distribution, and Fate of PCBs in the Environment.			5. Report Date: July 27, 1977 6.
7. Author(s): Frank C. Whitmore, Ph.D.			8. Performing Organization Rept. No. 474-361
9. Performing Organization Name and Address: Versar, Inc. 6621 Electronic Drive Springfield, Va. 22151			10. Project/Task/Work Unit No. Task 5 11. Contract/Grant No. 68-01-3259
12. Sponsoring Organization Name and Address: Office of Toxic Substances U.S. Environmental Protection Agency Washington, D.C. 20460			13. Type of Report & Period Covered: Final Task Report 14. 560/AX

15. Supplementary Notes

Project Officer: Thomas Kopp

16. Abstracts

A first order model for the sources, distribution and fate of PCBs in an aquatic system is described. The model is then applied to Lake Michigan and to the Great Lakes Systems. The results obtained from the model indicate that atmospheric sources are a major PCB input to the Great Lakes. Because of the great water mass of the lakes, the PCB concentration appears to be storage controlled rather than loss controlled. The major loss mechanisms are found to be co-evaporation from the air-water interface and entrapment with sediments. It is estimated that if all inputs of PCBs into Lake Michigan were eliminated, it would take more than 70 years for the concentration of PCBs in the water to decrease by 50 per cent.

17. Key Words and Document Analysis. 17a. Descriptors

Polychlorinated Biphenyls
Sediments
Water Chemistry
Sediment Water Interactions
Bioaccumulation
Adsorption
Air Pollution
Atmospheric Models
Watersheds
Water Pollution
Environmental Transport
Mass Transfer
Lakes
Precipitation Washout

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group

18. Availability Statement: Release Unlimited	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 180
	20. Security Class (This Page) UNCLASSIFIED	22. Price

FORM NTIS-35 (REV. 10-73) ENDORSED BY ANSI AND UNESCO. THIS FORM MAY BE REPRODUCED USCOMM-DC 8265-P74

Document is available to the public through the National Technical Information Service, Springfield, Virginia, 22151.

EPA 560/6-77-006

A FIRST ORDER MASS BALANCE MODEL FOR THE SOURCES, DISTRIBUTION AND FATE OF PCBs IN THE ENVIRONMENT

Final Task Report

Submitted to:

U. S. Environmental Protection Agency
Office of Toxic Substances
Special Projects Branch
Washington, D.C. 20460

Contract No. 68-01-3259
Task 5

Submitted by:

VERSAR INC.
6621 Electronic Drive
Springfield, Virginia 22151

July 31, 1977

This report has been reviewed by the Office of Toxic Substances, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

PREFACE

The continual patience and support of Mr. Thomas Rapp of the Office of Toxic Substances of the Environmental Protection Agency are gratefully acknowledged. Thanks are due to Carlos Fetterolf of the Great Lakes Fishery Commission for the opportunity to participate in the PCB Seminar-Dialogue held in Ann Arbor in May 1976, which allowed the exchange of views with Brock Neely and Dean Branson of Dow Chemical and Tom Murphy of DePaul University. The many suggestions that arose from several lengthy discussions with Ian Nisbet of Massachusetts Audubon Society, which have markedly increased the author's insight into modeling problems and the environmental properties of PCBs, are gratefully acknowledged. It is also a pleasure to acknowledge the efforts directed to a critical review of this document in its final form by Tom Murphy of DePaul University, by S. J. Kleinert of the Department of Natural Resources of the State of Wisconsin and finally by Brock Neely of the Dow Chemical Company. Needless to say errors in fact or in judgement that might remain are the sole responsibility of the author.

Finally, Section 6, which deals with a model of fish uptake and elimination of PCBs, was prepared by Steven Dental.

TABLE OF CONTENTS

		Page
EXECUTIVE SUMMARY		ii
1.0	INTEGRATION AND MASS BALANCE EQUATION	1
1.1	Mass Balance Model - General Considerations	2
1.2	Model Development	3
2.0	PARAMETERS FOR LAKE MICHIGAN	7
2.1	Introduction	7
2.2	General Physical and Hydrological Parameters for Lake Michigan	7
2.2.1	Biotic Mass, G, for Lake Michigan	8
2.3	Proportioning Constants, β and η	8
2.3.1	Biota Concentration Ratio, η	9
2.3.2	Sediment Concentration Ratio, β	9
2.4	PCB Input Rate to Lake Michigan	10
2.5	Evaporation Rate Constant K	11
2.6	Summary of Physical Parameters for Lake Michigan	11
3.0	APPLICATION OF MASS BALANCE EQUATION TO LAKE MICHIGAN	13
3.1	General Considerations	13
3.2	Integration of the Mass Balance Equation	15
3.2.1	The Sediment Load (M_{sed})	15
3.2.2	The Water Burden of PCBs (M_{water})	17
3.2.3	The Biotic Load of PCBs (M_{biota})	17
3.2.4	Outflow Loss Through Mackinac Straits ($M_{outflow}$)	17
3.2.5	Total Input and Cumulative Mass Balance (M_{total})	17
3.2.6	Co-Distillation Losses and K	18
3.3	Effect of Organic Content in Sediments	20
3.4	Extended Lake Michigan Model	21
3.4.1	N Sediment Zones	26
3.5	Effect of Suspended Solids	28
3.6	Effects to be Associated with PCB Loads Contained within Sediments	28
3.6.1	Redistribution Due to Complete Mixing of Water/Sediments	29
3.6.2	Effect of Layered Sediments - Undisturbed Sediments	32
3.6.3	Experimental Measurements on Re-solution	34
3.6.4	Final Word on Sediments	34

TABLE OF CONTENTS (CONT'D)

		Page
3.7	Effect on Aqueous PCB Concentration Due to Parametric Variation	35
	3.7.1 General Properties of the Mass Balance Equation	37
4.0	APPLICATION OF MASS BALANCE EQUATION TO GREAT LAKES SYSTEM	40
4.1	General Considerations	40
4.2	Lake Superior	45
4.3	Lake Michigan	45
4.4	Lake Huron	46
4.5	Lake Erie	47
4.6	Lake Ontario	48
4.7	Summary	49
4.8	Effect of Point Source Inputs	50
4.9	Comparison of Derived Results with Experimental Data	52
	4.9.1 Fallout on Lake Erie and Ontario	53
4.10	Effect of Gradient in B(t)	55
4.11	Effect of Regulatory Actions	55
5.0	CO-DISTILLATION AND THE EVAPORATION RATE CONSTANT K	56
5.1	Vapor Pressure of the Arochlors	57
	5.1.2 Self Evaporation Rates for Arochlor 1254	60
5.2	Calculation of the Evaporation Coefficient K for Lake Michigan	61
	5.2.1 Mass Balance at Lake Surface	61
	5.2.2 Effective Surface Vapor Pressure/Ultimate Solubility Ratio	65
5.3	Evaporation Rate Constant K	66
5.4	Comparison With Experiment	67
6.0	AN ESTIMATE OF THE PCB CONCENTRATION IN A TYPICAL LAKE TROUT WHEN EXPOSED TO AN AQUEOUS PCB CONCENTRATION	68
6.1	Development of the Model	68
6.2	Determination of the Rate Constants k_1 and k_2	70
6.3	Effect of Regulatory Actions on Trout PCB Concentrations	71
7.0	FURTHER WORK	77
7.1	Introduction of Environmental Degradation	78
7.2	Airborne Reservoir and the Generation of a Gradient in Fallout	79
7.3	Introduction of Spatial (or Temporal) Variation of Sediment	81
7.4	The Surface Layer and Co-Distillation	82

TABLE OF CONTENTS (Cont'd)

		Page
APPENDIX A: MATHEMATICAL CONSIDERATIONS		
A.1.0	GENERAL	A-1
A.1.1	$\phi=0$	A-1
A.1.2	$\phi>0$	A-2
A.2.0	PARTICULAR APPLICATIONS TO PROBLEMS ENCOUNTERED	A-2
A.3.0	APPLICATION OF EQUATION (A-6) (A-7)	A-3
A.4.0	EMPIRICAL EQUATIONS	A-5
A.5.0	METHODS OF SOLUTION OF EQUATION (A-3)	A-6
APPENDIX B: PARTITION COEFFICIENTS FOR AQUEOUS PCB SOLUTIONS		
B.1.0	INTRODUCTION	B-1
B.2.0	MEASUREMENT OF PARTITION COEFFICIENT	B-1
B.3.0	TYPICAL PARTITION COEFFICIENTS FOR PCBs	B-2
B.3.1	Aqueous/Activated Carbon	B-2
B.3.2	Aqueous/Soils and Clays	B-3
B.3.3	Aquatic Concentration Factors	B-3
B.3.4	Sediment Concentration Factors	B-4
B.3.5	Effect of Organic Content of Sediment on PCB Partition	B-4
APPENDIX C: ENVIRONMENTAL PCB LOAD		
C.1.0	INTRODUCTION	C-1
C.1.1	Empirical Description of Production, Sales and Specific Use Categories	C-1
C.1.1.1	Period 1930-1970	C-1
C.1.2	Period 1971-1979	C-3
C.2.0	ENVIRONMENTAL LOAD OF PCBs	C-4
C.2.1	Introduction	C-4
C.2.2	Total Environmental PCB Load, $M_{EV}(t)$	C-4
C.2.3	Effect of Monsanto's Voluntary Ban on PCB Sales	C-8
C.2.3.1	Comparison of the Results of Equation (C-14) with the Estimates of Nisbet and Sarofim	C-8
C.3.1	General Considerations on Mobile PCBs - $M_{EV}(t)$)	C-10
C.3.2	Effect of the 1970 Ban on Mobile PCBs ($M_{EV}(t)$)	C-13

TABLE OF CONTENTS (Cont'd)

Page

APPENDIX D: CUMULATIVE ENVIRONMENTAL PCB LOAD AND AN ESTIMATE OF THE CHLORINE SPECTRUM OF FREE PCBs

D.1.0 INTRODUCTION D-1
D.2.0 PCB SALES BY END USE CATEGORY, PERIOD (1930-1975) D-1
D.3.0 PCB LOSSES TO THE ENVIRONMENT. D-7
D.4.0 ESTIMATED CHLORINE SPECTRUM OF FREE PCBs D-9

APPENDIX E: BACKGROUND DATA USED TO CONSTRUCT THE MODEL FOR PCBs IN LAKE MICHIGAN

REFERENCES. F-1

LIST OF TABLES

Table No.		Page
2.6-1	Physical and Hydrologic Constants for Lake Michigan	12
3.2-1	PCB Concentrations in Lake Michigan	16
3.2-2	Summary of PCB Mass Distribution	19
3.3-1	Effect of Organic Content of Sediment on δ	22
3.3-2	Effect of Organic Content of Sediment on Aqueous Concentration	23
4-1	Hydrological and Physical Data, Great Lakes	42
4.8-1	Effect of Point Sources on Lake Erie and Lake Ontario Estimated Aqueous Concentrations of PCBs	51
4.9-1	Estimated PCB Load in the Sediments of the Great Lakes	52
5.1.2-1	Half Evaporation Rates Aroclor 1254	60
5.1.2-2	α Values for Aroclor 1254 (Equation 5-4)	61
5.4-1	Bidleman and Olney Surface Concentration Data[44]	67
6.2-1	Estimates of k_1 (Uptake Rate Constant)	72
B.3-1	Partition Measurements - PCBs in Water/Carbon Granules	B-2
B.3-2	Partition Coefficients Aqueous PCB/Carbon	B-2
B.3-3	Calculated Partition Coefficients[4] for Aqueous Aroclor 1254	B-3
B.3-4	Accumulation of PCBs by Various Aquatic Organisms	B-3
B.3-5	PCB Percolating Studies	B-4
C.2.2-1	$M_{EV}(t)$ = Environmental Load	C-7
C.3.1-1	Estimated Total Environmental PCB Load $[M_{EV}(t)]$ and Mobile Environmental PCB Load in $[m_{EV}(t)]$	C-12
C.4.1-1	Parameter Values for Equation (C-23) and Equation (C-25)	C-15
D.2-1	Proportional Use Factors - PCBs	D-2
D.2-2	Use Categories Aroclor 1242	D-3
D.2-3	Use Categories Aroclor 1248	D-4

LIST OF TABLES (Con't)

Table No.		Page
D.2.4	Use Categories Aroclor 1254	D-5
D.2-5	Use Categories Aroclor 1260	D-6
D.3-1	Estimated Loss Factors for PCBs by End Use	D-7
D.3-2	PCB Environmental Load by Aroclor Type	D-8
D.4-1	Approximate Molecular Composition of Selected Aroclors	D-10
D.4-2	Cumulative Environmental PCB Load by Chlorine Content	D-11
D.4-3	Computed Spectrum of Chlorine Content for Wild PCBs	D-12
D.4-4	Chlorine Content of Aroclors and of Environmental PCBs	D-14
E-1	Concentration of PCBs in Sediments Along the Southwestern Shore of Lake Michigan (1970-1971)	E-1
E-2	Concentration of PCBs in Michigan Streams Tributary to Lake Michigan	E-3
E-3	PCBs Entering Lake Michigan From Known Industrial and STP Discharges	E-4
E-4	Concentration of PCBs in Reported Michigan STP Effluents Tributary to Lake Michigan	E-5
E-5	Concentration of PCBs in Reported Wisconsin Paper Plant Effluents Discharging to Green Bay (1974-75)	E-6
E-6	Concentration of PCBs in Reported Wisconsin Miscellaneous Industrial Effluents Discharged to Lake Michigan	E-7
E-7	Concentration of PCBs in Reported Wisconsin STP Effluents Discharged to Green Bay (1974-75)	E-8
E-8	Concentration of PCBs in Reported Indiana STP Effluents Tributary to Lake Michigan	E-9
E-9	Concentration of PCBs in Reported Illinois STP Effluents Discharging to Lake Michigan	E-10
E-10	Lake Michigan Basin Hydrology	E-11
E-11	Estimates of Fish Biomass in Lake Michigan (1972-73)	E-12
E-12	Representative PCB Measurement	E-13

LIST OF FIGURES

Figure No:		Page
3.1-1	Graphic Description of Model Described by Equation (1-7') . . .	14
3.5-1	Plot of $\frac{C_W'(t)}{C_W(t)}$ for $\rho_1 = 4 \times 10^3$	27
3.6.1-1	Effect of Complete Removal of External PCB Sources Coupled with Complete Resolution from Contaminated Sediments	30
3.7-1	Properties of Equation (1-9).	39
4.1-1	Schematic of Great Lakes Indicating Flow Connections	41
5.1-1	Replot of Vapor Pressure of Aroclors	58
5.1-2	Data in Table 5.1-1 Plotted for Low Temperature Vapor Pressure of Aroclor Mixtures	59
5.1.2-1	Mass Evaporation Rate Aroclor 1254 from Itself	62
6.1-1	Schematic Fish	68
6.3-1	Computer Plot of Equation (6-12)	74
7.2-1	Volume Element for Airborne Reservoir Computation	80
C.3-1	Estimate Wild PCBs, $M_{gv}(t)$ where $t = 0$, 1930	C-15
D.4-1	Estimate Average Chlorine Number for Wild PCBs	D-13
E-1	Locations of Sediment Sampling Stations	E-2

LIST OF SYMBOLS

A = Area of target lake (ft^2)
A' = Drainage area of target lake (ft^2)
$B(t)$ = Rate of PCB injection into system during year t (lbs/yr)
C_i = PCB concentration
C_{is} = Saturation concentration of PCB in water
$C_w(t)$ = Aqueous PCB concentration
D = Average sediment deposition rate (lbs $ft^{-2} yr^{-1}$)
E = Mass evaporation rate for water (lbs/yr)
G = Biota mass in target lake (lbs)
H = Area of target lake (ft^2)
K = Surface evaporation rate constant (lbs yr^{-1})
M_{biota} = Cumulative PCB load in the biota (lbs)
$M_{evap.}$ = Cumulative PCB loss due to evaporation (lbs)
$M_{outflow}$ = Cumulative PCB loss due to outflowing water (lbs)
$M_{sed.}$ = Cumulative PCB load in sediments (lbs)
M_{total} = Cumulative PCB load input to system under consideration
M_{water} = Cumulative PCB load in aqueous phase (lbs)
M_i = Molecular weight of PCB
M_l = Mass of PCB evaporated (lbs)
M_w = Molecular weight of water
P_{is} = Equilibrium vapor pressure of pure solute (PCB) (Mm Hg)
P_w = Equilibrium vapor pressure of water (Mm Hg)
Q = Water mass of the target lake (lbs)
q = Rate of aqueous outflow from target lake (lbs yr^{-1})
t = Time (years)
t_f = Final time (years)
u = Integration variable

LIST OF SYMBOLS (CONT'D)

α = Fraction of sediments that are organic

β = Effective time constant for changes in PCB concentration

η = Average biota partition coefficient

θ = Average sediment partition coefficient

$\rho_{\perp}$ = Average partition coefficient for inorganic portion of sediments

$\rho_{\parallel}$ = Average partition coefficient for organic portions of sediments

ρ_{ψ} = Average partition coefficient for suspended solids

ψ = Concentration of suspended solids

EXECUTIVE SUMMARY

The work reported herein was undertaken to document and interpret available information on the transport and distribution of polychlorinated biphenyls (PCBs) in the environment. The model and results obtained therefrom also perform several important functions of a more general nature - the processes by which refractory organic compounds are transported and distributed in the environment are illustrated, a basis for predicting future effects of such compounds is provided, and the types of data required to perform such analysis are identified. Specifically with regard to PCBs, the work should be of assistance in determining potential future hazards from PCBs (free, in landfills, and in use) and in assessing the benefits of proposed regulation and cleanup activities.

Ideally, a study of the physical and temporal processes involved in the wide dissemination of a chemical species should begin with a strong data base which illustrates the spatial and temporal distribution of the target compound. Unfortunately, the ability to accurately analyse environmental samples and the recognition of the possible dangerous effects of very low levels have been very late in coming. Because of these factors there does not presently exist such a body of data. On the other hand, the inherent danger of these materials to the biosphere precludes the slow and orderly acquisition of such a body of data. In view of the obvious need of some effective regulatory action, and in view of the dangers inherent in exercising such regulatory options in the absence of guidelines suggesting the possible effects of such actions, it was deemed appropriate to attempt the construction of a model describing the nature of the problem.

The work presented here, an extension of that reported in the Versar Task I report under Contract 68-01-1259,[39] represents an attempt to construct a plausible scenario, based on reasonable and explicit assumptions, that is capable of answering the question "How did it come about that a compound, such as the PCBs, is so wide spread an environmental contaminant?" The resulting work involves the construction of several mathematical descriptive models made necessary by the lack of historical data coupled with the absence of a large base of reliable

contemporary measurements. The work is made necessary since the measurements that do exist strongly suggest that the PCBs are a persistent menace to the biosphere and hence actions to control them cannot be delayed while a truly adequate data base is obtained.

The basic model is constructed on a mass balance principle; that is, all the PCB input to a restricted region of the lithosphere may be accounted for by "storage", that is by solution or by uptake on suspended solids and by uptake within the biota, with the remainder of the input PCBs being carried off by the "loss" processes consisting of surface co-distillation, carry off by outflowing streams and/or entrapment within the sediments.

The model is somewhat complicated by the necessity of an analytic expression for the PCB input rate as a function of time; i.e., the driving function. In the absence of a sufficient amount of data, a model has been constructed to account for the losses to the environment, the free or "wild" PCB load and finally for the atmospheric reservoir of PCBs. The actual relationship of the various parts of the model are shown in Figure 1.

Environmental Load Model

Appendix C and Appendix D deal with an attempt to determine the magnitude of the total environmental load, the free environmental load and the atmospheric reservoir of PCBs; all as functions of time.

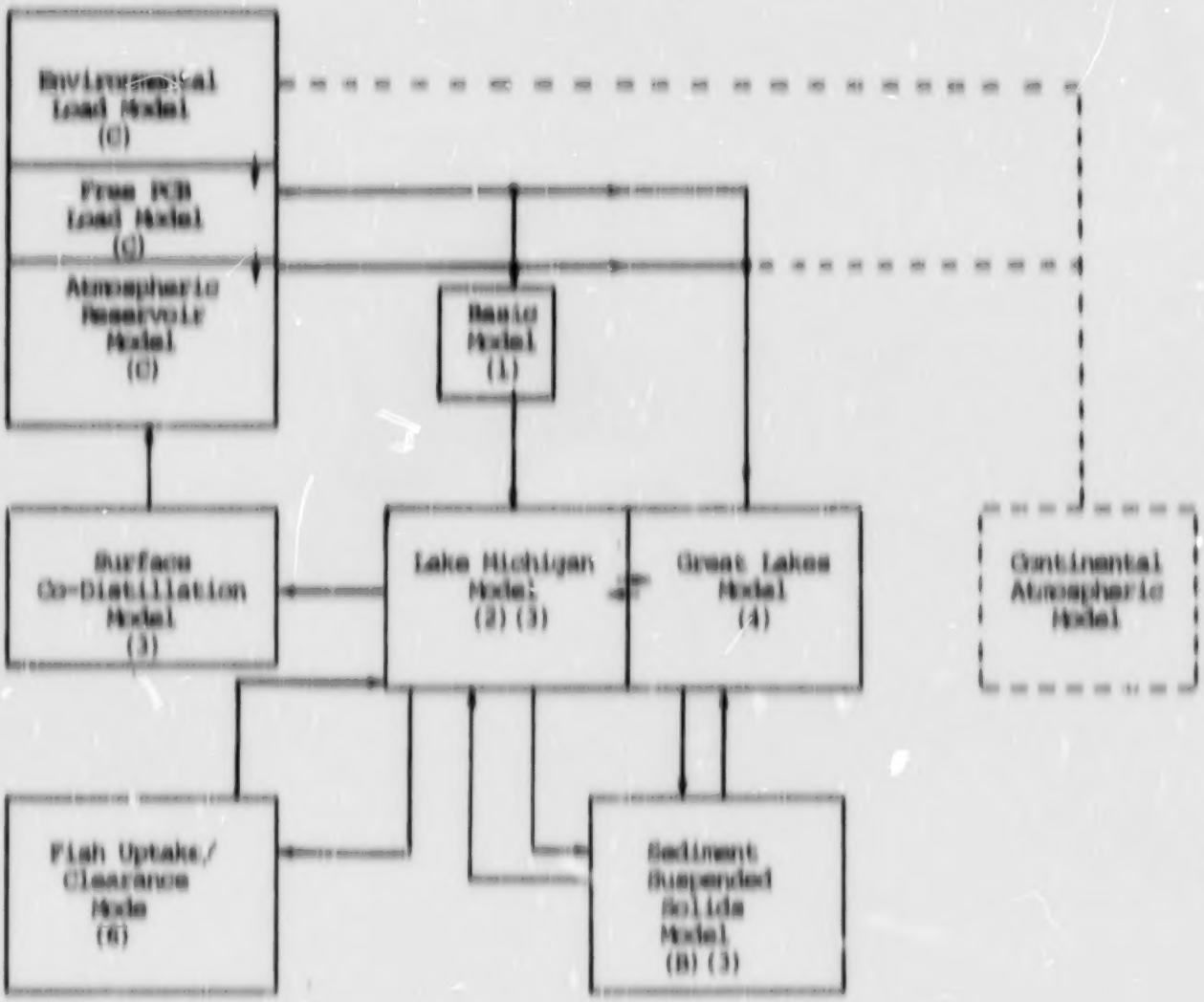
The results of this analysis are:

a. In 1975, the total environmental PCB load is estimated to be 1.76×10^9 lbs. within the continental United States.

b. In 1975, the total free or mobile PCB load in the continental United States is estimated to be 8.31×10^7 lbs. The balance of the total environmental load is deemed to be encapsulated in one form or another in landfills, for example.

Figure 1

Schematic Showing Relationship of the Various Sections of Report*


Environmental Load Model (C)
Free PCB Load Model (C)
Atmospheric Reservoir Model (C)
Basic Model (1)
Surface Co-Distillation Model (3)
Lake Michigan Model (2) (3)
Great Lakes Model (4)
Continental Atmospheric Model
Fish Uptake/ Clearance Rate (6)
Sediment Suspended Solids Model (B) (3)

*The number or letter associated with each block refers to section dealing directly with the subject matter.

c. As of 1970, the cumulative atmospheric reservoir contained some 6×10^7 lbs. of PCB indicating a rather rapid exchange between the total mobile PCBs and the atmospheric reservoir.

d. As of 1975, the PCB concentration in the air near Lake Michigan was of the order of 10 ng/m^3.

e. The estimated half life for fallout from the atmospheric reservoir is 0.9 years.

f. The average chlorine number for environmental PCBs is of the order of 4.32.

Mass Balance Equation as Applied to Lake Michigan

The results of this analysis are as follows:

a. The generation of a plausible scenario which arrives at a present day PCB concentration (water plus suspended solids) of the order of 7-10 ppt.

b. The assertion that atmospheric fallout constitutes the major input of PCBs to Lake Michigan.

c. Surface evaporation or co-distillation (the exact nomenclature is not known because the process is very incompletely understood) constitutes a significant PCB loss mechanism.

d. The presence of suspended solids within the water column can be expected to have a dominant effect on the actual (filtered) aqueous concentration.

e. The sediments should act as a significant sink for the removal of PCBs from the water column.

f. Even though there is considerable uncertainty as to the proper value for some of the important parameters, the sheer bulk of the water mass makes the aqueous concentration essentially independent of these parameters over wide ranges.

g. An estimate of 70 years to reduce the present PCB concentration by one-half in the absence of all external sources.

Application of the Mass Balance Model to the Entire Great Lakes System

a. The generation of a plausible scenario leading to the estimation of aqueous PCB concentrations which are within the range of measured values, i.e., less than 40 ppt.

b. The estimated average PCB concentration in the sediments of Lake Erie and Lake Ontario fall within an order of magnitude of other estimates[21].

c. The estimated fallouts in 1974 onto Lake Erie and Lake Ontario both fall within a few percent of other estimates[21].

d. Point source inputs, when introduced into Lake Erie and Lake Ontario lead to PCB concentrations in the aqueous phase as well within the sediments which are within a factor of 2 or 3 of direct observation.

e. An estimate of the life time of the present PCB loads in the absence of all sources.

Other Results

Other results obtained somewhat incidentally to the main effort include:

a. An estimate of the bioconcentration rates for PCBs for a trout of the order of 4×10^5.

b. An estimate that, for the trout, the uptake of PCBs from contaminated food is some 50 times more effective than from respiration.

c. The MacKay and Wolkoff[7] model for co-distillation is apparently not applicable in the situation where infalling PCB complicates the situation.

d. The suggestion that the significant difference in activity of PCBs in bulk solution compared to that in the surface layer is the driving force for the creation of a surface concentration gradient.

e. A formulation is developed that suggests the possibility of an analysis of the continental PCB atmospheric reservoir.

1.0 INTRODUCTION AND MASS BALANCE EQUATION

In order to discover the effect of various possible regulatory efforts on the distribution of refractory organics in the general environment, an attempt has been made to determine the manner in which a specific group of such compounds, PCBs, has become so widely dispersed, to determine the dynamics of the distribution process and to determine the changes in specific distribution that may be expected to result from several regulatory alternatives. Specifically, the effect of the voluntary ban introduced by Monsanto in 1970-71 can be demonstrated.

It would be most useful to construct a mathematical representation of a suitable segment of the environment based on the existence of large quantities of valid analytical data taken over a sufficiently long time interval so as to allow the reliable extrapolation of the important time effects. Unfortunately, the necessary data are not available. The recognition that PCBs were an environmental hazard came after their prolonged and widespread use in industry. In addition, the ability to analyse environmental samples for very low levels of PCBs is also a recent development. There has been too little time since the development of these sophisticated and exceedingly sensitive analytical techniques to have allowed anything like a complete spatial and temporal study of the levels of PCBs in any given region.

In view of the serious lack of a truly adequate data base, and because of the need to have at least a first order understanding of the physical processes involved in the transport and distribution of PCBs, an attempt has been made to construct a mathematical model which should contain at least a germ of the true situation. Specifically, the model serves to indicate something of the nature of the problem, and of the types of measurements that will be required to construct a truly satisfactory model to guide future regulatory activities.

To test the adequacy of the resulting mass balance model, it is first applied to Lake Michigan for which there exists a considerable body of information of late origin. The results of this analysis, on comparison with the observed PCB levels, serve as a basis for the detailed examination of some of the assumptions introduced into the model. Specifically, the effect of the organic content of the sediment and the phenomenon of co-distillation are examined in some detail.

In order to extrapolate the present day observations back into the past so as to illuminate the basic processes involved, it has been necessary to construct a relatively primitive model of the origin and dynamics of the free environmental load of PCBs. A significant guidepost in the construction of the free environmental load model is the observation that, at least in the recent past, the most significant PCB input route was through atmospheric fallout. Thus the environmental free PCB load model focuses attention on the origin and properties of the atmospheric reservoir.

Since the primary focus on aquatic pollution rests on the effect of such pollution on the living beings in the aquatic environment, some attention is paid to the construction of a simple fish-load model. Specifically, it can be shown that, for a trout, the body concentration of PCBs will follow that of the average aqueous concentration (with a suitable bioconcentration factor). Thus, in order to significantly reduce the PCB concentration within the higher predatory fishes it is essential to lower the aqueous PCB concentration correspondingly.

At the completion of the above consideration it is appropriate to further exercise the model by application to a schematic Great Lakes System. The results of this analysis are then compared to existing experimental data especially for Lake Ontario. The outcome of this comparison is the observation that, in spite of the necessity to make several assumptions, the theory is of some use since the same assumptions that suffice to deal with the simple system involving only Lake Michigan are found to be adequate to deal with the significantly more complex Great Lakes system.

Finally, the possible effects to be derived from various possible regulatory actions are discussed in terms of the model.

1.1 Mass Balance Model - General Considerations

In order to construct a mass balance model to be applied to a body of water such as Lake Michigan, it is appropriate to determine the manner in which an incremental increase in PCB content is distributed within the various processes available. In what follows, it is explicitly assumed that:

(a) Due to mixing and diffusional processes, the average aqueous PCB (refractory organic) within the body of water is dependent only on time.

(b) The PCBs (refractory organic) that review within the body of water are distributed by solution in the aqueous phase, in "solution" in the biota or within the sediment.

(c) The essential loss mechanisms from the body of water are evaporation from the air-water surface and carry-off due to outflowing waters, at least for short time intervals.

In terms of these assumptions, a differential equation can be developed that describes the time rate of change of the PCB concentration in the various phases of the lake in terms of the input rate of PCBs. This equation may be integrated under various assumptions as to the time dependence of the input rate to yield alternate expressions for the concentration of PCB within the separate phases as a function of time.

1.2 Model Development

Let B(t) be the rate of injection (lb/yr) of the PCBs from all sources at a reference time t (where t (years) = 0 in 1930). Then, within the interval t to t + Δt, an incremental amount of PCBs equal to B(t)Δt will be injected into the system. This quantity of PCBs will be partially partitioned into the various phases, with the balance removed by evaporation and/or outflow.

If Q(lbs) is taken to represent the total water mass in the lake (assumed to be constant) and $C_w(t)$ the concentration* of PCBs in the water

*In most cases concentration will be specified in gms solute/gm solution, i.e. as a dimensionless quantity. These exceptions will be explicitly stipulated when the occasion arises.

at time t, then

$$\frac{\Delta t}{\Delta E}\left[C_w(t+\Delta t) - C_w(t)\right] = \left(\frac{\Delta C_w}{\Delta E}\right)\Delta t$$

which, in terms of the definition of concentration, causes an increase in solutal PCB of magnitude*

$$\Delta m_w = Q\,\frac{\Delta C_w}{\Delta E}\,\Delta t; \qquad (1\text{-}1)$$

In a wide variety of environmental situations[1] there appears to exist a rather definite relationship between the concentration of PCBs within the sediment and/or the "average" member of the biota and that of the water in which they are immersed. These general relationships are herein defined as

$$\left.\begin{aligned} \rho &= \frac{C_{sed}}{C_{water}} \\ \eta &= \frac{C_{biota}}{C_{water}} \end{aligned}\right\} \qquad (1\text{-}2)$$

and are assumed to be independent of C_{water} and of time.

Using the relationships expressed by Eq. (1-2), the incremental increase in the mass of PCB stored in the biota is given as

$$\Delta m_{biota} = G\eta\,\frac{\Delta C_w}{\Delta E}\,\Delta t; \qquad (1\text{-}3)$$

where it is assumed that the concentration of PCBs within the biota was in equilibrium with that in the water at time t and that G(lbs), the total mass of the exposed biota, is constant over the period of interest.

Similarly, if the rate of deposition of sediments is taken to be D(lbs/ft^2/yr) and the area of the lake to be A(ft^2), then, assuming that the principal exchange processes between water and sediment occur within the aqueous phase during the settling out process, the incremental PCB pickup by the sediments is given as:

$$\Delta m_{sed} = AD\rho C_w(t)\Delta t \qquad (1\text{-}4)$$

*The term "solutal PCBs" is taken to represent the total PCBs in solution or attached to suspended sedimentary material.

where the additional term (1/2) $\frac{\Delta C}{\Delta t}\Delta t$ is considered small, especially as $\Delta t \to 0$.

If the rate of outflow from the lake (through the Straits of Mackinac is taken as Q (lbs/yr), then the loss of PCB due to this outflow may be taken as:

$$\Delta m_{outflow} = QC_w(t)\ \Delta t\ . \qquad (1\text{-}5)$$

Finally, the mass of PCB carried out of the system by evaporation is given as:

$$\Delta m_{evap} = KC_w(t)\Delta t \qquad (1\text{-}6)$$

where K is the evaporation rate constant which will be discussed below (Section 6).

Now, the principle of conservation of mass requires that all the injected PCB be accounted for, (note that no effective degradation processes are considered to be operative) from which it follows that

$$B(t)\Delta t = \Delta m_w + \Delta m_{biota} + \Delta m_{sed} + \Delta m_{outflow} + \Delta m_{evap}\ .$$

Introducing the definitions of each of the incremental mass loads, and proceeding to the limit $\Delta t \to 0$ and dropping the subscript w since the only concentration appearing is that of the PCB in water, the operative differential equation becomes

$$(Q + Gn)\frac{dC}{dt} + (S + K + \lambda V_D)C = B(t) \qquad (1\text{-}7)$$

which, for convenience in what follows, may be rewritten using the substitutions,

$$\left.\begin{aligned} \beta &= \frac{S + K + \lambda V_D}{Q + Gn} \\ \gamma &= \frac{1}{Q + Gn} \end{aligned}\right\} \qquad (1\text{-}8)$$

and Equation (1-7) becomes

$$\frac{dC(t)}{dt} + \beta C(t) = \gamma B(t)\ , \qquad (1\text{-}7')$$

The solution of Equation (1-7) takes the simple explicit form

$$C(t_f) = \gamma e^{-\beta t_f} \int_0^{t_f} B(u) e^{\beta u} du \qquad (1-9)$$

under the special circumstances that $C(t) = 0$ at $t = 0$ (1910) and further that the parameters γ and β (and hence the constants introduced in Equation 1-1 through 1-6) are independent of time.

In the initial application of the model in Sections 3.1 and 3.2, it is further assumed that:

(a) There are no degradation processes that are active for PCBs over the time interval in question.

(b) That all the PCBs may be treated as a single chemical species.

(c) That both γ and β are independent of position as well as of time.

The further development of the general mass balance model, in the latter sections of Chapter 3 deals with the effect on the solution of Equation (1-9) due to spatial variations in γ and β as well as the effects of suspended solids. In Sections 4.9.1 and 4.10, the effect of a spatial variation in $B(u)$ is considered. Finally, the effect of environmental degradation of PCBs on the forcing function $B(u)$ and hence on the solution of Equation (1-9) is discussed.

The next two chapters deal with the application of the model to a typical test case; i.e., to the study of PCB distribution in Lake Michigan.

3.0 PARAMETERS FOR LAKE MICHIGAN

3.1 Introduction

As shown in Section 3.7, the solution of the mass balance equation is rather insensitive to the precise value of β, at least in terms of a direct comparison to the available *in situ* aqueous concentration measurements. Nevertheless, it is altogether appropriate to attempt an estimate of the parameters, α, η, G and K. In most cases, since an accurate value cannot be assigned for these parameters, an average value will have to be used with full recognition that, although the detailed results may well be modified as better data become available, the general features of the model should still be applicable. In later sections, an attempt will be made to estimate the range of uncertainty in the computed PCB concentrations in terms of the possible ranges of the significant parameters.

3.2 General Physical and Hydrological Parameters for Lake Michigan

The general physical and hydrological parameters for Lake Michigan are taken as follows:[2]

A = surface area of the lake = 6.24×10^{11} ft^2
S = outflow through Straits of Mackinac = 1.2×10^{13} lb/yr
Q = water mass in lake = 1.1×10^{15} lbs
D = sediment deposition rate = 0.204 lbs/ft^2 yr
A^1 = average drainage area = 1.29×10^{11} ft^2

3.2.1 Biotic Mass, G, for Lake Michigan

A representative value for the biomass in lake Michigan, recognising the relatively limited data that are available on specific species and the absence of a detailed ecological pyramid, may be obtained from the estimates contained in Table E-11 (Appendix E).

In view of the uncertainties in the details of the relative magnitudes of the various levels of the biological pyramid, an estimate of

$$G = 10^{13} \text{ lbs},$$

is taken for what follows. At the same time, it is perfectly possible that G might actually be as much as an order of magnitude higher. Further, it is assumed that $G \neq \beta(t)$ and, thus, has remained constant over the time interval of interest.

3.3 Proportioning Constants, ρ and η

In order to determine the most appropriate values for the proportionality constants ρ and η, in the absence of a well-founded theoretical explanation of the physical processes which determine them, it is necessary to rely on in-situ measurements of concentration over wide regions of the target water body to establish reasonable statistical reliability. Actually, such a body of data does not exist for Lake Michigan at this time. On the other hand, some data do exist for Lake Ontario which should allow at least a reasonable estimate of the appropriate values for Lake Michigan.

The essential experimental problem lies in the observed fact that although the concentration of PCBs in typical contaminated sediments and in the larger fishes lie well within the range of high accuracy for analysis, the corresponding water levels lie very near the present limits of detection. Thus, since the proportioning constants are expressed as ratios of PCB concentrations, the uncertainty in $C_w(t)$ will necessarily show up as uncertainties in the values of ρ and η. But again, the relative insensitivity of $C_w(t)$ to the precise value of β, suggests that even these uncertainties are not of impressive significance to the derived results.

2.3.1 Biota Concentration Ratio, η

The brief summary of data displayed in Table E-12 and the discussion which follows in Section E-5, both of Appendix E, suggests that the value to be used for the bioconcentration ratio, η, is

$$\eta \approx (4\text{-}8) \times 10^5$$

for Lake Ontario which, by inference, should also apply to Lake Michigan. It should be noted that η is taken as an average concentration ratio over all members of the biota; thus, there will be specific species showing considerable variation from the assumed value.

Since the basic physical processes that account for this partitioning of PCB-like materials should be independent of the actual concentration of PCBs in the aqueous phase (so long as the aqueous solution is less than saturated), it is reasonable to assume that η is independent of time.

2.3.2 Sediment Concentration Ratio, ρ

The estimates of sediment concentration as compared to water concentration that are discussed in Section E.6 of Appendix E suggest an average value for ρ as applied to Lake Michigan of

$$\rho \approx 2 \times 10^4.$$

This result is also subject to considerable variation, even over the confines of a single body of water. For example, due to influent effects, there may be considerable spatial variation in the properties of the sediment. In a typical sediment, some portion, α, of the sediment is organic in nature; the remainder, $(1-\alpha)$, is inorganic. The reported values of partition coefficients for organic and for inorganic material as compared to water are very different (as discussed in more detail in Appendix B).

Let ρ_o = the average partition coefficient organic/water
ρ_i = the average partition coefficient inorganic/water
α = organic fraction,

then

$$\rho_{eff} = \alpha\rho_o + (1-\alpha)\,\rho_i. \qquad (2\text{-}1)$$

In Appendix B, typical values of ρ_0 and ρ_1 are derived from published experimental data. The implications of a spatial variation in α and thus in ρ_{eff} are discussed in Section 3-4. Suffice it to say again, that the insensitivity of β to the precise value of the proportioning parameters suggests that the average value selected will suffice until more comprehensive aqueous concentration data are available for comparison.

2.4 PCB Input Data to Lake Michigan

Again, the lack of historical data imposes the necessity for the introduction of an assumption. Specifically, it is assumed that the rate of PCB input to Lake Michigan follows essentially the same time dependence as does the estimated environmental load as given by Equation (C-24) (Appendix C) and more specifically by Equation (C-40) (Appendix C). The available background data for the period 1971-1974 on tributary inputs to the lake are presented in Tables (E-2) through (E-9) of Appendix E.

A variety of fallout rate measurements have been reported[3] indicating rates as high as 0.5 lbs/mi^2/yr = 87 µg/m^2/yr in the heavily industrialized portion of Sweden [4] to the other extreme of 17.5 µg/m^2/yr observed in Iceland.[5] In view of the rather heavy concentration of industry in the Lake Michigan area, it will be assumed that the average fallout in the 1974 era was 50 µg/m^2/yr.**

Thus, taking the area of the lake to be 5.8×10^{10} m^2, the annual fallout should be of the order of

$$B_{\text{fallout direct}} \simeq 6.4 \times 10^3 \text{ lbs/yr in 1974.}$$

Thus, the contribution to the PCB input 1971-1974 may be summarized as follows:

Point sources	1.6×10^3 lbs/yr	
Lake fallout	6.4×10^3 lbs/yr	
Basin fallout	5.4×10^3 lbs/yr	(where it is assumed that 50 percent of basin fallout actually enters the lake)[6] *
Total	13.4×10^3 lbs/yr	(1973-1974).

*The fraction of material which falls on the watershed to ultimately end up in the lake depends markedly on the soil type of the watershed as well as the compound in question. In the absence of other guides, the factor 50 percent is selected.
**Treated in more detail in Section 4.9.

As shown in Appendix C,

$$B(t) = at^{1.5}$$

which for the reference year, 1974, was estimated to be

$$13.4 \times 10^3 = a(44)^{1.5}$$
$$a = .0237$$

so that, in what follows,

$$B(t) = 0.0237t^{1.5}. \qquad (2\text{-}2)$$

2.5 Evaporation Rate Constant K

This factor is the most difficult parameter to establish, primarily since the theory of co-distillation has received little attention. An attempt to apply the theory of MacKay and Wolkoff[7] in the special situation of dynamic equilibrium between fallout input, evaporation and diffusion within the surface layer is presented in Section 6. In the meantime a tentative value for K is assigned as follows

$$K = 3.2 \times 10^{12} \text{ lbs/yr.}$$

In Section 3, the mass balance equation will be used to determine a more "correct" value for K. Section 5 will deal with K in more detail.

2.6 Summary of Physical Parameters for Lake Michigan

The parametric values listed in Sections 2.2 through 2.4 are summarized in Table 2.6-1.

---

*The discussion in Section 2.4 and in Appendix E specifically neglects the large cumulative spill due to the local industry in the Waukegan Harbor federal navigation channel - a spill amounting to more than 100,000 lbs (USEPA Survey, 16 Sept. 1976 contained in letter from C. M. Timm). The PCB concentration in the outflowing waters at the north breakwater light were found to be less than background levels (0.1 µg/kg) and thus most of this large spill is apparently confined to the sediments within the channel. Thus, even though this is a large PCB reservoir, it is not taken into account in the total Lake Michigan PCB economy. See further discussion in Appendix E.

Table 2.6-1*

Physical and Hydrologic Constants for Lake Michigan

The values used for the various physical and hydrologic constants for Lake Michigan are listed below:[8]

A = surface area of the lake = 6.24×10^{11} ft^2

S = outflow through Strait of Mackinac = 1.2×10^{15} lb/yr

Q = water mass in lake = 1.1×10^{18} lbs

D = sediment deposition rate = 0.204 lbs/ft^2/yr

η = biota/water concentration ratio = 4×10^5

ρ = sediment/water concentration ratio = 2×10^4

B (1974) = PCB input rate in 1974 = 1.34×10^9 lbs

R = evaporation rate constant = 2.2×10^{14} lbs/yr
[this assumption will be discussed below in Section 5]

Then, from the data above, the various factors appearing in Equation (1-9') may be evaluated as follows:

$$A\rho D = 2.25 \times 10^{10} \text{ lbs/yr}$$

$$Q + \rho\eta = 1.14 \times 10^{18} \text{ (lbs)}, \quad (Q + \rho\eta)^{-1} = 8.77 \times 10^{-19} \text{ (lbs)}^{-1}$$

$$S + R + A\rho D = 5.7 \times 10^{13} \text{ lbs/yr}$$

$$\lambda = \frac{S + R + A\rho D}{Q + \rho\eta} = 0.05 \text{ (yr)}^{-1}$$

$$\gamma = \frac{\lambda}{A + \rho\eta} = 8.77 \times 10^{-19} \text{ (lbs)}^{-1},$$

*A discussion of the effect of variation of the parameters Q, η and R is found in Section 3.7.

3.0 APPLICATION OF THE MASS BALANCE EQUATION TO LAKE MICHIGAN

3.1 General Considerations

The mass balance equation (1-9), which is derived from the schematic representation shown in Figure 3-1-1, may now be solved for Lake Michigan using the parametric data presented in Chapter 2. Several comments are in order as to the effect of the assumptions outlined in Chapter 1. For explicitness, the model is carried through assuming that there is no spatial variation in the driving function B(t) and that there are no active degradation processes causing the removal of PCBs. Actually both these assumptions may be relaxed as shown in Chapter 7.

Further, the assumption that all PCB's may be treated as a single chemical species is not really necessary in the sense that the parameters η, μ and κ may, or perhaps should, be treated as averages over the various species of PCB that are involved. An interesting result of the enormous mass of water involved in a body such as Lake Michigan is shown in the discussion in Section 3.7 which clearly shows the insensitivity of the solution of Equation (1-9) to the precise values of the parameters.

The explicit assumptions:

(a) Evaporation, or more accurately, co-distillation is a significant process having marked influence on the mass balance and,

(b) the parameters β and γ are time independent; seem to be irreducible, at least in this first order model.

Finally, the assumption of uniformity of aqueous concentration may be removed by a simple modification of the method of solution applied to the schematic Great Lakes System contained in Chapter 4.

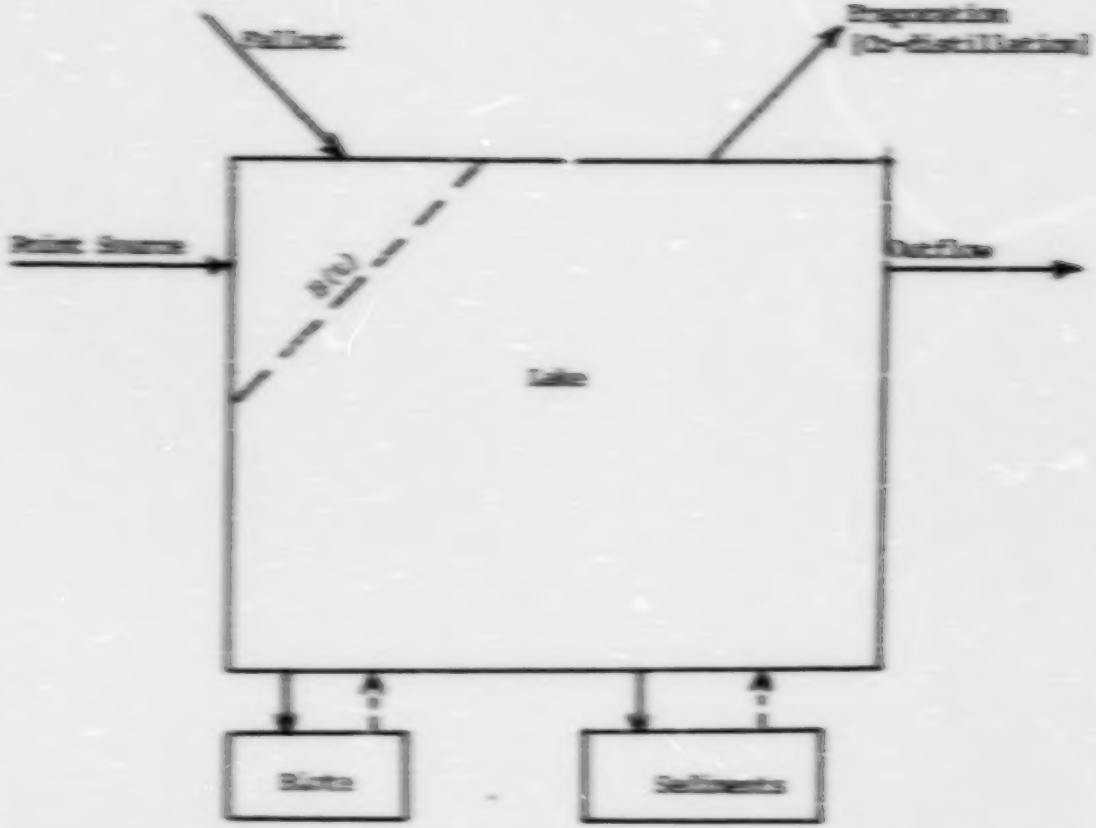


Figure 1.1-1
Graphic Description of Model Described
by Equation (1-7)

3.2 Integration of the Mass Balance Equation

In terms of the parameters for the lake and the assumed form for B(t) from Equation (2-2), the differential equation for C(t), Equation (1-9) becomes:

$$C(t_f) = 2.08 \times 10^{-19}\, e^{-0.035 t_f} \int_0^{t_f} u^{3.5}\, e^{0.035u}\, du \qquad (3\text{-}1)$$

which can be integrated by normal numerical methods but can more conveniently be integrated by the methods outlined in Appendix A. In any case, the approximate result of integration of Equation (3-1) is

$$C_w(t_f) \simeq 4.44 \times 10^{-19}\, t_f^{3.5}\, e^{-0.035 t_f} \qquad (3\text{-}2)$$

which, for (1975) (t_f = 45 years) yields an aqueous PCB concentration estimate of 8.5×10^{-12} (8.5 ppt). The detailed results of the numerical evaluation of Equation (3-2) are displayed in Table 3.2-1.

To now examine the implication of Equation (3.1) it is useful to determine the distribution of PCBs within the various portions of the lake as of 1975.

3.2.1 The Sediment Load (M_{sed})

From the definition of the incremental sediment pickup, Equation (1-4), the total sediment load in 1975 is given by (t_f = 45 years)

$$M_{sed}\ (1975) = A\Delta u \int_0^{45} C_w(t)\, dt \qquad (3\text{-}3)$$

which, on substitution of Equation (3-2) and integration yields

$$M_{sed}\ (1975) = \underline{1.56 \times 10^{9}\ \text{lbs}} = \underline{7.81\ \text{tons}}\ . \qquad (3\text{-}4)$$

TABLE 3.3-1

PCB Concentrations in Lake Michigan[a]
(Equation 3.2)

Date	t_f (years)	$C_w(t_f)\left(\frac{gm}{gm}\right)$	$C_w(t_f)$ (ppt)
1930	0	0	0
1935	5	5.56×10^{-15}	6×10^{-3}
1940	10	1.3×10^{-14}	0.013
1945	15	7.72×10^{-14}	0.077
1950	20	2.71×10^{-13}	0.27
1955	25	7.1×10^{-13}	0.71
1960	30	1.55×10^{-12}	1.55
1965	35	2.98×10^{-12}	2.98
1970	40	5.22×10^{-12}	5.22
1975	45	8.52×10^{-12}	8.52

[a]Measurements in 1973 indicate a range of aqueous concentration of 1 to 7.5 ppt[9]

3.2.2 The Water Burden of PCBs (M_{water})

The total PCB mass that is in solution in 1975 is given by

$$M_{water}(1975) = Q \times C_w(45)$$

$$= 1.1 \times 10^{14} \times 8.52 \times 10^{-16} = \underline{9.37 \times 10^{2}} \text{ lbs} . \qquad (3\text{-}5)$$

3.2.3 The Biotic load of PCBs (M_{biota})

The biotic load of PCBs in 1975 is given by

$$M_{biota}(1975) = cn \times C_w(45) = \underline{3.41 \times 10^{3}} \text{ lbs} . \qquad (3\text{-}6)$$

3.2.4 Outflow Loss Through Mackinac Straits ($M_{outflow}$)

From the definition of the effect of the outflowing current S, Equation (1-6), the cumulative PCB loss due to this factor may be estimated as

$$M_{outflow} = S \int_0^{45} C_w(t)dt = \underline{8.34 \times 10^{3}} \text{ lbs} . \qquad (3\text{-}7)$$

3.2.5 Total Input and Cumulative Mass Balance (M_{total})

The total cumulative PCB mass that entered the lake is given by

$$M_{total} = \int_0^{45} B(t)dt$$

which, on substitution of the form of B(t) from Equation (2-1), yields the result

$$M_{total} = .0237 \int_0^{45} e^{.1t} \, dt$$

$$= \underline{1.49 \times 10^{4}} \text{ lbs} , \qquad (3\text{-}8)$$

If now the sum of Equation (3-4),(3-5),(3-6) and (3-7) is compared to (3-8) the result shows that the net loss due to evaporation was (cumulative)

$$\underline{2.40 \times 10^{4}} \text{ lbs} . \qquad (3\text{-}9)$$

3.2.6 Co-Distillation Losses and K

From Equation (3-2) and the definition of the average of a function,[10] the average concentration (1930-1975) is given by

$$\bar{C}_w(t) = \frac{4.44 \times 10^{-19}}{45} \int_0^{45} u^{0.6} e^{-\cdots\cdots u} dw \qquad (3\text{-}10)$$

which, on integration (the exponential may be expanded in Maclaurin series retaining only the first two terms), yields the approximate solution

$$\bar{C}_w(t) = \frac{4.44 \times 10^{-19}}{45} \left(\frac{45)^{0.6}}{0.6}\right) e^{-\cdots\cdots} \cdots$$

$$= 1.64 \times 10^{-12} , \qquad (3\text{-}11)$$

Thus, from the definition of K, Equation (1-6), the average value of K is given as

$$K = \frac{(\Delta M_{evap})_{total}}{\bar{C}_w(t)\Delta t} = \frac{2.4 \times 10^5}{1.64 \times 10^{-12}} \times \frac{1}{45} = \underline{3.25 \times 10^{15} \text{ lbs/yr}} \qquad (3\text{-}12)$$

which is then to be compared with the assumed value of K (Table 2.5-1) of 2.2×10^{15} lbs/yr.

A further estimate of the value of K may be determined by examination of the incremental changes in PCB load in each of the "phases" during the period 1974-1975.

$$\Delta M_w = Q\Delta C_w = 8.36 \times 10^4 \text{ lbs}$$

$$\Delta M_B = Q\kappa\Delta C_w = 3.04 \times 10^3 \text{ lbs}$$

$$\Delta M_{exit} = \bar{Q}\bar{C}_w = 9.76 \times 10^4 \text{ lbs}$$

$$\Delta M_{sed} = AD_1\bar{C}_w = 1.83 \times 10^3 \text{ lbs}$$

where, from Equation (3-2), the average concentration for the period 1974-1975 was

$$\bar{C}_w(t)_{1974\text{-}1975} = \underline{8.12 \times 10^{-12}}$$

Table 3.2-3

Summary of PCB Mass Distribution*

	Cumulative	1974-1975
M_{input}	1.45×10^5 lbs.	1.39×10^5 lbs.
M_{water}	9.37×10^3 lbs.	8.36×10^3 lbs.
M_{sed}	1.56×10^5 lbs.	1.83×10^3 lbs.
M_{biota}	3.41×10^3 lbs.	3.04×10^2 lbs.
$M_{outflow}$	8.34×10^3 lbs.	9.76×10^2 lbs.
Net $M_{evap.}$	2.395×10^5 lbs.	2.43×10^3 lbs.
	$\bar{R} = 3.25 \times 10^{15}$ lbs/yr	$\bar{R} = 2.99 \times 10^{15}$ lbs/yr

*Summary of results of Section 3.2.1 through 3.2.5.

and the change in concentration during the same period

$$\Delta C_w(t)_{1974\text{-}1975} = \underline{0.78 \times 10^{-11}} \ .$$

Furthermore, the input to the lake system during this same time interval was

$$\Delta M_{input} = .0237 \int_0^{45} t^{3.5} dt$$

$$= \underline{1.19 \times 10^5} \text{ lbs} \ .$$

Hence, the net loss of PCBs due to evaporation during the period 1974-1975 is equal to the net input less the accounted for deposition in the other "phases"; i.e.

$$\Delta M_{evap_{1974\text{-}1975}} = \underline{2.43 \times 10^4} \text{ lbs}$$

whereupon

$$K = \frac{2.43 \times 10^4}{8.12 \times 10^{-11}} = 2.99 \times 10^{15} \text{ lbs/year} \ . \qquad (3\text{-}13)$$

A further discussion of the K values, Equation (3-12) and (3-13), will follow later; in the meantime another important parameter must be dealt with.

3.3 Effect of Organic Content in Sediments

Returning to the formal solution of the mass balance equation, Equation (1-9) and the definitions in Equation (1-8), which will be rewritten here for convenience

$$C_w(t_f) = \gamma e^{-\beta t_f} \int_0^{t_f} B(u) e^{\beta u} du \qquad (1\text{-}9)$$

and

$$\left.\begin{aligned} \beta &= \frac{S + K + AD_0}{Q + D_1} \\ \gamma &= \frac{1}{Q + D_1} \end{aligned}\right\} , \qquad (1\text{-}8)$$

It has been shown in Section (1-5) that the effect of variation of the decay constant β, is to produce rather small changes in the resulting concentration. Specifically, from Equation (2-1), it is found that the value of ρ to be used in a given situation depends markedly on the organic fraction α of the sediment. In Appendix B, it is demonstrated that appropriate values for $\rho_c \approx 10^5$ and for $\rho_i = 10$, so that the specific value of ρ_{eff} may vary from 10 for entirely inorganic sediments to 10^5 for entirely organic sediments. Table 3.3-1 illustrates the effect of organic content on ρ_{eff} and thence on β. In addition, the effect of variation in organic content on the resulting concentration to be expected in Lake Michigan is summarized in Table 3.3-2.

3.4 Interim Lake Michigan Model

Suppose that the lake actually consists of two distinct regions in that the organic content of the sediments are very different in the two regions. The lake may then be divided into two segments, denoted by I and II with rapid interchange between the aqueous portions of the segment such that the aqueous concentrations are identical at all times. Thus, the mass balance equation for the segments becomes:

$$\left.\begin{aligned} \left|Q_1 + \Omega_1\eta\right| \frac{dC_1(t)}{dt} + \left|S_1 + K_1 + DA_1\rho_1\right| C_1(t) &= B_1(t) \\ \left|Q_2 + \Omega_2\eta\right| \frac{dC_2(t)}{dt} + \left|S_2 + K_2 + DA_2\rho_2\right| C_2(t) &= B_2(t) \end{aligned}\right\} \qquad (3\text{-}15)$$

but, $C_1(t) = C_2(t)$, $\left|Q_1 + \Omega_1\eta\right| + \left|Q_2 + \Omega_2\eta\right| = Q + \Omega\eta$,

$S_1 + S_2 = S$

$K_1 + K_2 = K$

and $B_1(t) + B_2(t) = B(t)$.

Adding the Equations (3-15) yields the resulting overall mass balance equation

$$\left|Q + \Omega\eta\right| \frac{dC(t)}{dt} + \left|S + K + D\left(A_1\rho_1 + A_2\rho_2\right)\right| C(t) = B(t), \qquad (3\text{-}16)$$

TABLE 3.3-1

Effect of Organic Content of Sediment on δ

q	ρ_{eff}	$\Delta\rho_{eff}$	δ (Eq. 1-8)
0.001	10^3	1.27×10^{11}	.0314
0.01	10^4	1.27×10^{10}	.0404
0.1	10^5	1.27×10^{9}	.1417
1.0	10^6	1.27×10^{8}	1.145

TABLE 3.3-2

Effect of Organic Content of Sediment on Aqueous Concentration

ρ_{eff}	λ	C_0	$C_{20\ yrs}$ (ppt)	$C_{30\ yrs}$ (ppt)	$C_{40\ yrs}$ (ppt)	$C_{45\ yrs}$ (ppt)
0	.0298	0	.297	1.76	6.13	10.17
10	.0298	0	.297	1.76	6.13	10.17
10^2	.0314	0	.29	1.67	5.70	9.39
10^3	.0404	0	.28	1.61	5.43	8.87
5×10^3	.0853	0	.25	1.28	4.01	6.30
10^4	.1417	0	.19	0.91	2.52	3.77
10^5	1.145	0	.004*	0.003*	0.001*	0.003*

* Because of convergence problems these values are to be considered as essentially zero.

As before

$$\left.\begin{aligned} \beta &= \frac{E + R + D\,(A_{12}\ell_1 + A_{21}\ell_2)}{Q + DV} \\ \gamma &= \frac{1}{Q + DV} \end{aligned}\right\} \qquad (3\text{-}17)$$

Equation (3-16) has the formal solution

$$C_w(t) = \gamma e^{-\beta t_f} \int_0^{t_f} e^{\beta u} B(u)\, du$$

where u is a symbolic integration variable. On substitution of the values for γ and the form of B(u) from Equation (2-1):

$$C_w(t) = 2.08 \times 10^{-14}\, e^{-\beta t_f} \int_0^{t_f} e^{\beta u} u^{4.5}\, du\,. \qquad (3\text{-}18)$$

Now, the values of t_f which are of interest are in the range

$$0 \le t_f \le 45 \qquad (1930\text{-}1975)$$

hence, the series solution of Equation (3-18) can be shown to converge sufficiently rapidly to be of practicable value

$$\beta \le 0.4\,.$$

By suitable manipulation of the defining equation for β, Equation (3-17), it can be shown in the case that the areas of the two segments of the lake are equal,

$$\beta_{eff} = .0298 + 5.6 \times 10^{-5}(\rho_1 + \rho_2), \qquad (3\text{-}20)$$

Now, by way of illustration select

$\rho_1 = 10$, i.e. entirely inorganic sediment

$\rho_2 = 4 \times 10^4$, i.e., 4% organic matter in sediment

*The average organic content of Lake Michigan sediments is of the order of 4% (actually this is based on a total organic carbon measurement), (11)

then

$$\beta = 0.0823$$

and, suitable evaluation of Equation (3-18) for this specific value of β yields the approximate form for $C_w(t)$

$$C_w(t) = 4.62 \times 10^{-19} t^{3.5} e^{-.0823t} \qquad (3\text{-}21)$$

from which $C_w(1975) = 8.49 \times 10^{-11}$ (which compares favorably with the values tabulated in Table 3.3-2). Hence, the total mass balance may be computed (for the period 1930-1975) as follows:

$$\left.\begin{aligned} \Delta M_{water} &= GF_w'(45) \\ \Delta M_{biota} &= GnC_w(45) \end{aligned}\right| = 1.14 \times 10^{13} \times 8.45 \times 10^{-11} = \underline{9.68 \times 10^{2}} \text{ lbs}$$

$$\Delta M_{outflow} = \beta \int C_w(t)dt = 1.2 \times 10^{13} \times 6.89 \times 10^{-11} = \underline{8.27 \times 10^{2}} \text{ lbs}$$

$$\Delta M_{sed_1} = \frac{AD}{2} \rho_1 \int C_w(t)dt = \frac{6.24 \times 10^{11} \times .204}{2} (10) \times 6.89 \times 10^{-11} = \underline{43.85} \text{ lbs}$$

$$\Delta M_{sed_2} = \frac{AD}{2} \rho_2 \int C_w(t)dt = \underline{1.75 \times 10^{3}} \text{ lbs}$$

and the total input is as before (Equation 3-10)

$$\Delta M_{input} = \underline{1.45 \times 10^{3}} \text{ lbs} .$$

Hence, the evaporation loss is, in this case,

$$\Delta M_{evap} \approx \underline{2.24 \times 10^{3}} \text{ lbs}$$

which is to be compared to the value obtained in Equation (3-9).

The special significance of the large variation in PCB partition coefficient allowed for each of the two zones is demonstrated by a computation of the average concentration of the sediment deposited during 1975 for each of the two zones.

$$\text{PCB conc}_{sed} = \frac{M_{(PCB)\ sed}}{\text{deposited mass}} = \frac{M_{sed_i}}{A_i D_i}$$

where

A_i = area covered (assumed to be $\frac{A}{2}$)

D_i = deposition rate = 0.204 lbs/ft^2/yr
(assumed to be uniform over the entire lake).

In zone I, $\rho = 10$ (no organic)

$$\overline{C_i}_{sed(1975)} = \frac{44}{6.37 \times 10^{11}} = 6.91 \times 10^{-11}$$

$$\overline{C_i}_{sed(1975} = \frac{1.75 \times 10^{5}}{6.37 \times 10^{11}} = 2.75 \times 10^{-7}.$$

Thus, in this case, the relative concentration within the sediment in the two zones differ by several orders of magnitude. The total sediment load is approximately 1.75×10^5 lbs to be compared to the value listed in Equation (3-4).

3.4.1 N Sediment Zones

To extend the model to a system partitioned into N zones of differing sediment constitution (i.e., different percentage of organic material) it is only necessary to replace the factor $A\rho$ which occurs in δ by the sum

$$\sum_{i=1}^{N} A_i D_i \rho_i \qquad (3\text{-}12)$$

where provisions have been included to provide for varying deposition rates, D_i.

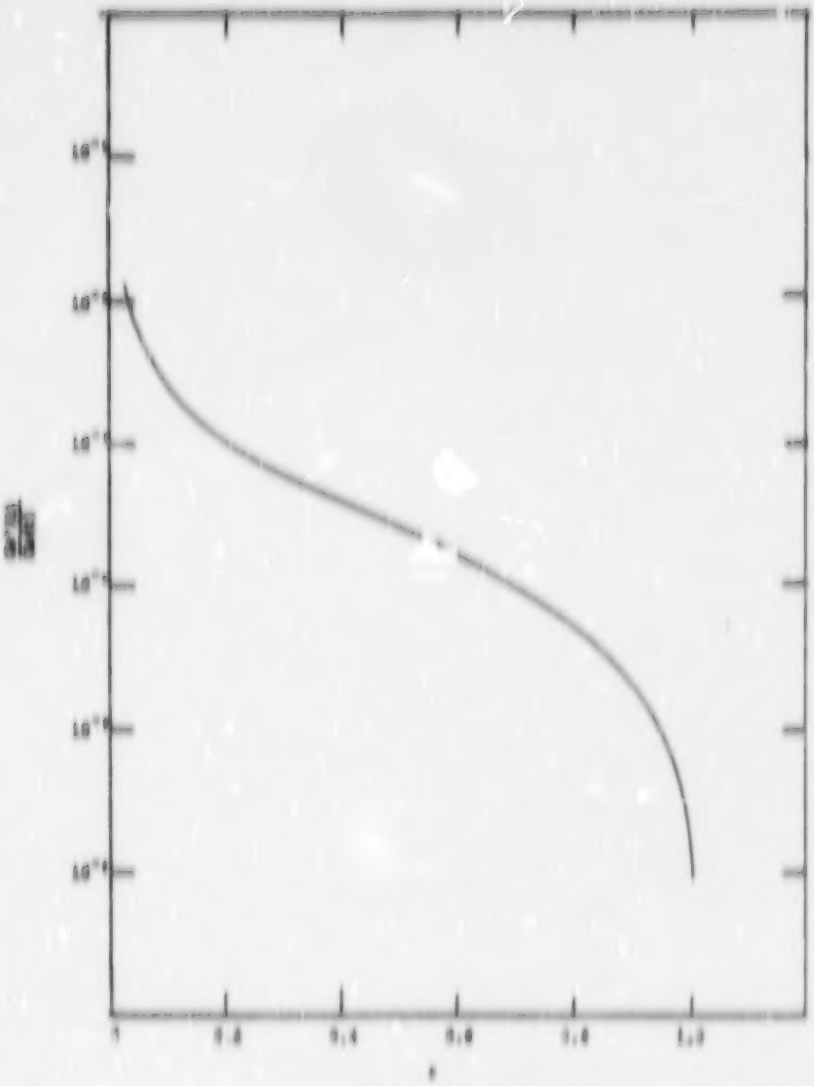


Figure 3.9-1

Plot of $\frac{\Delta W'(t)}{\Delta W(t)}$ for $\beta_1 = 4 \times 10^3$

(Equation 3.56)

3.5 Effect of Suspended Solids

Suppose that there exists a concentration ψ of permanently suspended solids characterized by a partition coefficient ρ_ψ within the body of water of mass Q. Then the total mass of water plus sediments is

$$M = Q(1+\psi), \tag{3-23}$$

If now the concentration within a filtered water sample were $C_w'(t)$ then that associated with the suspended solids would be $\rho_\psi C_w'(t)$ and the total mass of "solubed" PCB would be given as

$$M(t)_{PCB\ Sol} = Q(1+\psi\rho_\psi)C_w'(t), \tag{3-24}$$

On the other hand, the effective concentration of the PCBs within the suspension as given by Equation (3-2) for Lake Michigan is taken as $C_w(t)$ and the mass of PCB within the suspension is

$$M(t)_{PCB\ Sol} = QC_w(t). \tag{3-25}$$

Equating Equation [illegible] with (3-25) indicates that

$$C_w'(t) = \frac{C_w(t)}{(1+\psi\rho_\psi)}. \tag{3-26}$$

Hence, given the suspended solids concentration and the percentage of organic material contained therein, it is possible through Equation (3-26) to relate the $C_w(t)$ from Equation (3-2) with the actual measured $C_w'(t)$ of filtered aqueous solutions.

3.6 Effects to be Associated with PCB Loads Contained within Sediments

One serious question that might arise deals with the possible effect of re-solution of entrapped PCBs from sediments deposited during an earlier epoch. It has been asserted[12] that one nasty effect to be associated with attempts to eliminate sources of PCBs to such bodies as the Great Lakes lies in the fact that the sediments contain large reservoirs of PCBs which would have to be removed prior to any lessening of the aqueous concentration within the lake. Several comments on this question are appropriate.

3.6.1 Redistribution Due to Complete Mixing of Water/Sediments

Suppose that at the end of 1976, all external sources of PCB to Lake Michigan were suppressed and, further, that all the PCBs stored in the sedimentary layers were available for re-solution. What could be expected to be the time before the aqueous concentration fell to 50 percent of its 1976 level?

It is assumed that the partition coefficient between water and the sediment is 3×10^5 (as assumed before) and that the sediment rate is $AD = 1.27 \times 10^{11}$ lbs/year and has been constant during the entire interval from 1930, then the total PCB load at the end of 1976 within the sediment is given as

$$M_{sed(PCB)} = AD\rho \int_0^{46} C_w(t) = \underline{1.32 \times 10^9} \text{ lbs} \qquad (3\text{-}27)$$

where $C_w(t)dt$ is given by Equation (3-2). Also, at the end of 1976, the total load in the aqueous plus biotic phases is given by

$$M_{PCB}(w) = (Q + Gn)C_w(46) = \underline{1.06 \times 10^9} \text{ lbs} \qquad (3\text{-}28)$$

thus, the total "available" PCBs is 2.38×10^9 lbs at the reference date. To compute the resulting concentration in the water after mixing

$$C_w(46)_{eff} = \frac{M_{PCB}(46)}{A\delta pt + (Q + Gn)}$$

where $A\delta pt = (A\delta p(46)$ = total mass of contaminated sediment.

Thus, immediately after mixing the aqueous concentration will be

$$C_w(46)_{eff} = 10.3 \times 10^{-12},$$

During the succeeding year, the losses from the system resulting from evaporation plus outflow are given as

$$M_{loss} = (R + G)\bar{C} \text{ lbs/year.}$$

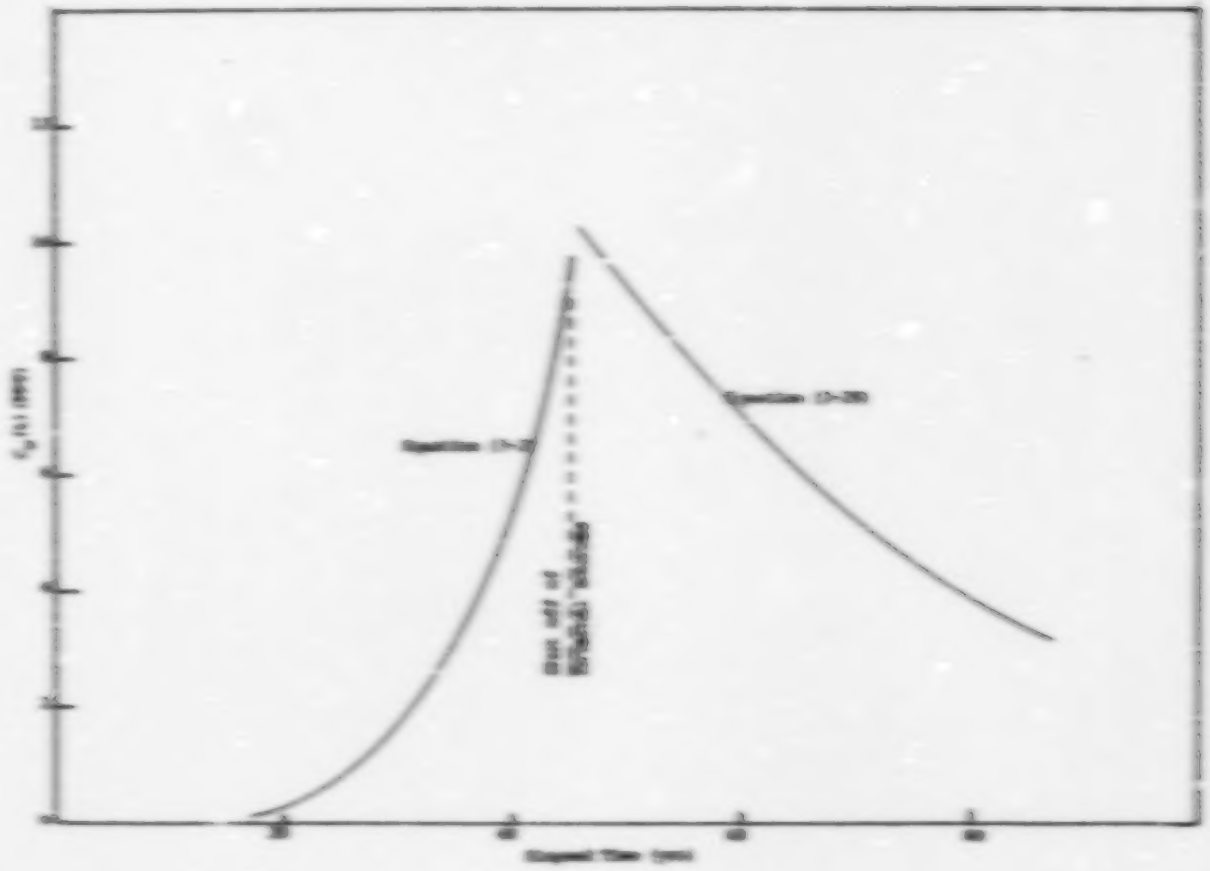


Figure 3.6.1-1

Effect of Complete Removal of External PCB Source
Coupled with Complete Resolution from Contaminated Sediments

To a first approximation then

$$M_{loss}(47\ year) = (3.4 \times 10^{-1})(C_w(46)) = \underline{3.5 \times 10^{3}}\ lbs,$$

thus, the remaining PCB is just $2.38 \times 10^{5} - 3.5 \times 10^{3} = 2.345 \times 10^{5}$ lbs. Meanwhile, the sediment load has increased by an amount $\Delta D = 1.27 \times 10^{11}$ lbs, so that the concentration in the water at the end of the 47th year is approximately

$$C_w(47) = 10.0 \times 10^{-12},$$

Proceeding in this stepwise manner results in the following approximate concentrations in succeeding years as given in Table 3.6.1-1.

TABLE 3.6.1-1
ESTIMATED AQUEOUS CONCENTRATION IN LAKE MICHIGAN

t (for t - 1930)	Concentration
46	10.3×10^{-12}
47	10.0×10^{-12}
48	9.78×10^{-12}
49	9.53×10^{-12}
50	9.30×10^{-12}
51	9.08×10^{-12}
52	8.86×10^{-12}
53	8.65×10^{-12}
54	8.45×10^{-12}

In order to best utilize the results obtained above, a standard regression analysis yields the relationship (see Appendix A)

$$C_w(t) = 1.115 \times 10^{-9}\ t^{-1.223} \qquad (3\text{-}29)$$

where t in years is measured from 1930. From Equation (3-29), the approximate time required for the aqueous concentration to be reduced to 50% of its value in 1976, is

$$t_{1/2} = 76.5\ years,\ i.e.\ 2052.5\ calendar\ date.$$

3.6.2 Effect of Layered Sediments - Undisturbed Sediments

The above calculation is highly simplified in the sense that the situation within the sediment is such that only a small part of the entire PCB load would be available for resolution in an undisturbed sediment. Actually, the sediment must be considered as being made up of layers deposited in earlier epochs each with a concentration appropriate to the aqueous concentration during the time of deposition. Under these circumstances, it would be expected that diffusion of the PCBs would tend to diminish the concentration gradient with the result that the top (most recent) layer would, in fact, exhibit a concentration less than would be expected as a result of the aqueous concentration at the time of its formation. To illustrate the effect of diffusion on reduction of the concentration gradient through the various layers of the sediment, consider the expression for the rate of mass transport along a concentration gradient[13]

$$\frac{dm}{dt} = DA\left|\frac{C_2-C_1}{d}\right|, \qquad (3\text{-}30)$$

where A is the area of the layer (cm^2) of thickness d (cm) across which there exists a concentration (gm/cm^3) difference C_2-C_1. D is the diffusion coefficient ($\frac{cm^2}{sec}$) of the solute in the solution. Applying Equation (4-3) to Lake Michigan sediments during the period 1930-1975, the parameters of use are

$$\begin{aligned} A &= 5.8 \times 10^{13}\ cm^2 \\ b &= 5\ cm\ (0.1\ cm/year)^{[14]} \\ C_1 &= 0 \\ C_2 &= 2.8 \times 10^{-9}\ gm/cm^3\ \text{(from Equation (3.2) with suitable change in dimensions)} \end{aligned}$$

In order to estimate D, it is noted that[15] typical diffusion coefficients for organics in water are of the order of 10^{-5} cm^2/sec or, in terms of t in years, $D = 3.5\ \frac{cm^2}{year}$. Substitution of the numerical value into Equation (3-30) yields

$$\frac{dm}{dt}\ (gm/yr) = 2.29 \times 10^5\ lbs/yr. \qquad (3\text{-}31)$$

The value deduced from Equation (3-11) is obviously much greater than the total available sediment load; a result that can only be understood if it is assumed that, due to this diffusion, the actual concentration of the surface layer is significantly below that specified as due to the aqueous concentrations. Without undertaking the complex problem of applying the diffusion equation in its differential form to the problem, it is evident that on the time scale involved herein, the concentration within the total layered sediment should tend to some uniform value which would be expected to be below the average value for the precipitated layers over the period (1930-1975); lower than the average since the layers deposited prior to the earliest injection of PCBs (1930) were originally at zero concentration of PCBs. The result to be expected from all this is that, essentially, the PCBs contained within the sediments are actually not available and hence, in the event that all external sources were shut off, the only processes active would be the losses due to outflow, to evaporation and to the material carried off by the newly forming sediments. Under these circumstances, the applicable differential Equation is Equation (1-7) with $B(t) = 0$

$$\frac{dC}{dt} + \delta C = 0$$

for which the solution is

$$C = C_0 e^{-\delta t}, \qquad (3\text{-}12)$$

Introducing the value of $\delta = 0.05$, the time required for $C(t)$ to fall to $1/2$ its value in 1975 is

$$t_{1/2} = 13.7 \text{ years, i.e. in 1987-1988 area!}$$

3.6.3 Experimental Measurements on Re-solution

In a laboratory study of a number of sediment samples from Lake Michigan, among other sources, Fulk et al [16] report that as a consequence of resuspension of PCB contaminated sediments in water

a. The amount of soluble pesticide material added to the water column by disposal of the sediment interstitial water is negligible at sediment-to-water ratios of 1:10 or less.

b. The amount of pesticide (material) desorbed from suspended solids is negligible at sediment-to-water ratios of 1:10 or less."

In view of these observations it would appear that, in the absence of residual suspended solids which contain PCBs from the sediment, that the estimates of the previous two sections of this report tend to exaggerate the effect of re-suspension of the sediment.

3.6.4 Final Word on Sediments

It can be inferred from the above that, in the absence of some catastrophic event involving the re-suspension of the complete contaminated sediments, PCBs that have been carried down with forming sediments are, for all intents and purposes, permanently removed from participation in future contamination processes. This observation can be expected to be significantly less forceful when applied to the moving sediments in a river since re-suspension is often a significant process.[17]

A further point in the context of sediment re-solution is in order. In those cases wherein the sediments are essentially undisturbed, the further formation of new sediment should, in the event that the aqueous concentration (through which they are transferred to the bottom) is decreasing in time, further isolate the more heavily contaminated sediments.

All in all, it appears that, in the absence of significant natural or biological degradation processes, sediment fixation is the primary process acting to remove PCBs from active participation in biological processes.

3.7 Effect on Aqueous PCB Concentration Due to Parametric Variation

As pointed out above the parameters G, η and K have been assigned somewhat arbitrary values. It is important to note that the time constant θ, defined by Equation (1-8), directly affects the numerical value of the computed aqueous PCB concentrations as is shown by the solution of the mass balance Equation (see Equation A-9). It thus becomes important to discuss the possible range of the parameters G, η and K, and the variations introduced in the computed PCB concentrations that result from the extreme situations.

The average biological portion coefficient, η, has been taken to be 4×10^6 but, depending on the nature of the biota could easily be significantly different. For the purposes of this analysis,

$$1 \times 10^6 \leq \eta \leq 8 \times 10^7 \qquad (3\text{-}33)$$

It has been suggested[14] that the total mass of the biota, G, which has been taken as 10^{10} lbs, could very well be an order of magnitude greater, that is,

$$10^{10} \leq G \leq 10^{11} \qquad (3\text{-}34)$$

Finally, the parameter K, which is the surface co-distillation rate constant has been more or less arbitrarily assigned a value of 2.3 lbs/yr. Actual mass balance computations, in Section 3.2.5 suggest a value for K of the order of 3.0×10^{15} lbs/yr. Further, the theory of co-distillation of MacKay and Wolkoff,[7] if applied directly to the situation in Lake Michigan, suggests that K might be as high as 3×10^{15} lbs/yr. Thus, the possible range of K is

$$0 \leq K \leq 3 \times 10^{15} \qquad (3\text{-}35)$$

where, if K = 0, there is no loss of PCB through the surface to the air column above.

The other parameters, Q, A, D, and B which appear in β are established parameters. The remaining parameter ρ, which characterizes the sediment partitioning is established by the organic content of the sediment and is treated in some detail in Section 3.3.

Returning to the definition of β,

$$\beta = \frac{K + B + AD\rho}{Q + (Q_1)} \qquad (3\text{-}6)$$

it is clear that the minimum value of β occurs when K = 0, (Q_1) is maximum; i.e.,

$$\beta_{min} = \frac{B + AD\rho}{Q + (Q_1)_{max}} = 0.0075 \quad . \qquad (3\text{-}36)$$

On the other hand, the maximum value of β would occur when K is maximum and (Q_1) is minimum, i.e.,

$$\beta_{max} = \frac{K_{max} + B + AD\rho}{Q + (Q_1)_{min}} = 3.75 \qquad (3\text{-}37)$$

Compelling arguments, presented in Section 5.2, indicate that the MacKay and Wolkoff[7] theory of co-distillation cannot apply without modification in a situation wherein there exists a surface layer of enhanced concentration. Thus, it would seem that the upper bound on K is of the order of 5×10^{13} lbs/yr, hence the maximum value for β

$$\beta_{max} = 0.049$$

Summarizing the above, the probable range of β for Lake Michigan is

$$0.0075 \leq \beta \leq 0.049 \quad . \qquad (3\text{-}38)$$

The situation for β near the lower limit could be characterized as storage dominated in that the factor $(Q + Q_1)$ is significantly larger than the loss factor $(K + B + AD\rho)$. The upper bound for β may, with some justification, be referred to as loss dominated.

3.2.1 General Properties of the Mass Balance Equation

From the form of Equation (1-9) it can be seen that, if there were to exist an equilibrium state then $\frac{dC}{dt} = 0$. Hence, from Equation (1-9)

$$\beta C = \gamma B(t)$$

$$\text{or} \quad C_{eq} = \frac{\gamma}{\beta} B(t), \tag{3-10}$$

But B(t) is a function of t, hence

$$\frac{dC_{eq}}{dt} = \frac{\gamma}{\beta} \frac{d}{dt} [B(t)] \neq 0, \text{ hence}$$

the system cannot be in equilibrium unless B(t) is no longer time dependent. Further, in the special case that $B(t) = 0$ after $t \geq t_0$, then Equation (1-9) becomes, for $t \geq t_0$,

$$\frac{dC}{dt} + \beta C = 0,$$

$$\text{or} \quad C(t>t_0) = C(t_0)e^{-\beta(t-t_0)}. \tag{3-11}$$

From the form of Equation (1-11) it is clear that β is the effective time constant of the system.

The general solution of Equation (1-9), given in Appendix A, is of the form

$$C(t) = \gamma a t_0^{\delta+1} \sum_{n=0}^{N} (-1)^n \frac{(\beta t)^n}{n!(\delta+1+n)}, \tag{A-9}$$

where $B(t) = at^{\delta}$, (C-40)

In the following section an attempt is made to determine the proper magnitude of the two partition coefficients, ρ and η and to estimate the total biomass, Ω as well as the evaporation rate constant K, all in order to determine the appropriate value for β as defined by Equation (3-8). It is instructive to examine the effect of various values of β on the solution of Equation (A-9) as follows:

$$C(t)\left[\gamma\alpha t_F^{\delta+1}\right]^{-1} = \sum_{n=0}^{\infty}(-1)^n \frac{(\beta t)^n}{\Gamma(\delta+1+n)} \tag{3-12}$$

which can be evaluated for $0 \leq \beta \leq 0.1$ and for $t = 45$ years. The results of this calculation are shown in Figure 3.2-1.

Further,

$$\frac{\partial C(t)}{\partial \beta}\left[\gamma\alpha t_F^{\delta+1}\right]^{-1} = \frac{1}{\beta}\sum_{n=0}^{\infty}(-1)^n \frac{n(\beta t)^n}{\Gamma(\delta+1+n)}, \tag{3-13}$$

$$\frac{\partial^2 C(t)}{\partial \beta^2}\left[\gamma\alpha t_F^{\delta+1}\right]^{-1} = \frac{1}{\beta^2}\sum_{n=0}^{\infty}(-1)^n \frac{n(n-1)(\beta t)^n}{\Gamma(\delta+1+n)} \tag{3-14}$$

In a manner similar to the evaluation of Equation (3-12), Equations (3-13) and (3-14) have been evaluated for $t = 45$, $0 \leq \beta \leq 0.1$ with the results presented in Figure 3.7.1-1.

Clearly, the effect of β, within the range $0 \leq \beta \leq 0.1$, is such that the maximum excursion in $C(45)$ for the extremes of the range of β is the order of 16 per cent. When one recognises that the bulk of the available data may easily have uncertainties of the order of 16 per cent, it is clear that the present situation does not demand high precision in the determination of the various parameters of the system.

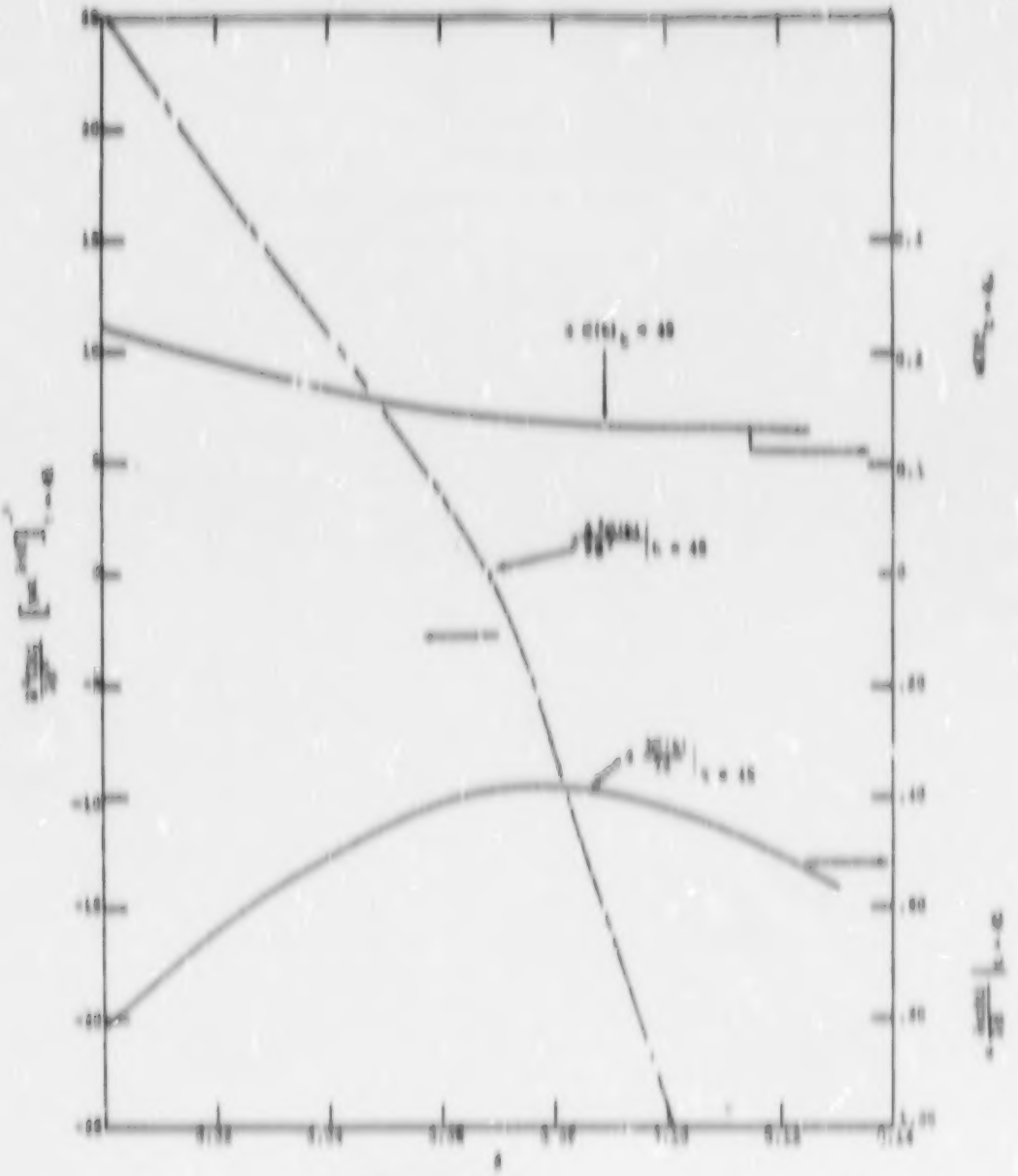


Figure 3.7-1
Properties of Equation (1-9)

4.0 APPLICATION OF MASS BALANCE EQUATION TO GREAT LAKES SYSTEM

4.1 General Considerations

The detailed procedure to be applied to the entire Great Lakes System follows exactly that used for Lake Michigan with due account being taken of the interconnection between the lakes. A decided difficulty arises when it is noted that there is very little data available to allow an estimate of the biological mass, B, for the lakes other than Michigan. In order to obtain some useful approximation for the biotic masses, it has been assumed that the total biotic mass of each lake is proportional to its surface area. Thus, the values given under the heading Bn in Table 4-1 were derived from the estimated biotic mass of Lake Michigan.

In a similar manner, the evaporation rate constant K was derived. Since the thermodynamic theory of co-distillation [7] indicates that the rate of evaporation of the solute (PCB) is proportional to the water mass evaporation rate and that the proportionality factor depends on physical constants, it is appropriate to derive the K values for the lakes from that found in Lake Michigan, allowance being made for the individual water mass evaporation rates (E_j).

The physical and biological data [18] appropriate to the lakes are listed in Table 4-1 which follows. For each individual lake, it is assumed that the input PCB is the sum of the fallout contribution plus the inflowing streams from the upper contaminated lakes. Point sources are neglected, except insofar as they contribute to the fallout itself. Then the general differential equation for each lake is given by

$$(A + Bn)_j \frac{dC_j(t)}{dt} + (K + E + AD_0)_j C_j(t) = B_j(t) + \sum_{(i)}^{n} E_{ij} C_i(t) \qquad (4\text{-}1)$$

where the E_{ij} represent the inflowing contaminated streams with concentration $C_i(t)$; and the $B_j(t)$ represents the PCB input due to fallout on the lake plus runoff from the drainage basin. The subscript j will take on values S, M, H, E, O which represent the initial letter for the name of the individual lakes.

The solution of equation (4-1) where $C_j(t) = 0$ at $t = 0$, is given as

$$C_j(t) = \frac{1}{(Q + QR)_j} e^{-\beta_j t_\ell} \int_0^{t_\ell} \left\{ B_j(u) + \sum_{i=1}^{n} a_{ij} C_i(u) \right\} e^{\beta_j u} \, du \qquad (4\text{-}2)$$

where

$\beta_j = \frac{(R + S + A)\alpha_j}{(Q + QR)_j}$ where the elements of β are listed in Table 4-1

and where u is simply an integration variable, $u = t$.

Now, the geographic conditions that obtain in the Great Lakes are illustrated in the schematic, Figure 4-1.1, which follows:

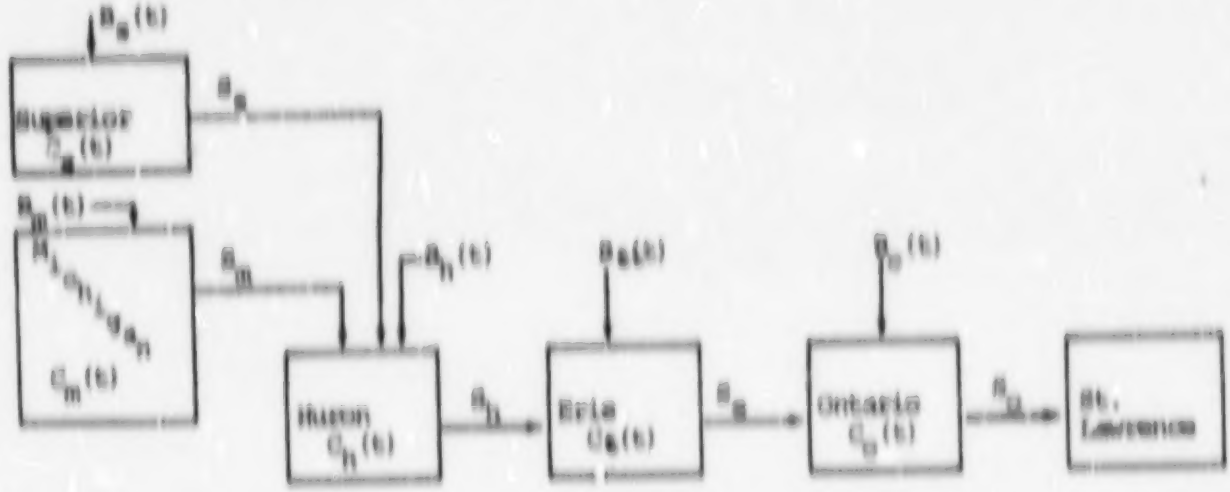


Figure 4.1-1

Schematic of Great Lakes

Indicating Flow Connections

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Thus, from Figure 4.1-1 it is clear that Equation (4-2) for Lake Superior and Lake Michigan assumes the simplified form

$$C_j(t) = \frac{1}{(Q + QR)_j} e^{-\theta_j(t)} \int_0^t B_j(u) e^{\theta_j(u)} du \qquad (4\text{-}3)$$

where $j = s, m$.

For Lake Superior, using the data in Table 4.1-1

$$C_s(t) = \frac{1}{2.76 \times 10^{14}} e^{-1.0000 t} \int_0^t B_s(u) e^{1.0000 u} du \qquad (4\text{-}4)$$

$$\text{then,} \quad C_s(t) = 3.62 \times 10^{-15} e^{-1.0000 t} \int_0^t B_s(u) e^{1.0000 u} du. \qquad (4\text{-}4)$$

There remains to determine a proper form for $B_s(t)$ as follows:

If it is assumed that the fallout in 1974 was 50 $ug/m^2/yr = 1.023 \times 10^{-6}$ $lb/ft^2/yr$ (i.e. = not a function of latitude)

then
$$B_s(44) = 2.06 \times 10^5 \text{ lbs}$$
$$B_m(44) = 1.60 \times 10^5 \text{ lbs}$$
$$B_h(44) = 1.72 \times 10^5 \text{ lbs}$$
$$B_e(44) = 6.63 \times 10^4 \text{ lbs}$$
$$B_o(44) = 7.08 \times 10^4 \text{ lbs}.$$

If the form of $B_j(t) = a_j t^{1.5}$, then the proper values of the a_j's are as follows:

$$a_s = .0365$$
$$a_m = .0283$$
$$a_h = .0305$$
$$a_e = .0117$$
$$a_o = .0125.$$

4.0 Lake Superior

In terms of the defined input functions, Equation (4-4) may be written as

$$C_s(t) = 1.32 \times 10^{-14} e^{-.0005t} \int_0^t u^{1.5} e^{.0005u} du$$

which has the solution (see Appendix A for details)

$$C_s(t) = 2.93 \times 10^{-10} t^{1.5} e^{-.0005t}, \qquad (4\text{-}4)$$

To check mass balance, note that the total input in the interval 1930-1974, is given by

$$Q_{in} = \int_0^t B(\ )du = \int_0^{44} .0365u^{1.5} du = \underline{2.23 \times 10^5} \text{ lbs.}$$

On the other hand, the total losses are given by

$$Q_{loss} = (Ab + R + B) \int_0^t C_s(u) du$$

$$= \underline{1.727 \times 10^5} \text{ lbs.}$$

while the stored PCB is given by

$$(Q + Qh) C_s(44) = (6.84 \times 10^{-11})(2.787 \times 10^{15})$$

$$= \underline{1.787 \times 10^5}$$

or total input = $\underline{2.23 \times 10^5}$ lbs; amount accounted for is $\underline{3.16 \times 10^5}$ lbs.

4.3 Lake Michigan

$$C_m(t) = \frac{1}{(Q+\Omega V)_m} e^{-\beta_m(t)} \int_0^t R_m(u) e^{\beta_m(u)} du$$

which, in terms of the numerical values in Table 4.1, yields the form

$$C_m(t) = 8.96 \times 10^{-17} e^{-.0005t} \int_0^t (.0283) u^{1.5} e^{.0005u} du$$

$$= 2.54 \times 10^{-18} e^{-.0005t} \int_0^t u^{1.5} e^{.0005u} du$$

for which the approximate solution is[a]

$$C_m(t) = 5.64 \times 10^{-19} e^{-.0005t} t^{2.5}, \qquad (4\text{-}6)$$

Again, check the mass balance,

$$Q_{in} = \int_0^{44} R_m(t)\,dt = \underline{1.56 \times 10^5} \text{ lbs.}$$

The net loss = $(R + S + A\Omega_0) \int_0^t C_m(t)\,dt = \underline{4.999 \times 10^4}$ lbs.

and the stored material = $(Q + \Omega V) C_m(44) = \underline{1.052 \times 10^5}$ lbs.

Hence, total input = 1.56×10^5 lbs, total accounted for is 1.552×10^5 lbs.

---

[a]Results in this section differ slightly from those derived in Section 3.2. Since R is taken $R = 3 \times 10^{12}$ lbs/yr.

4.4 Lake Huron

Since Lake Huron is seen to have two additional inputs, from Lake Superior and from Lake Michigan, the solution for $C_h(t)$ takes the general form

$$C_h(t) = \frac{1}{(Q + QR)_h} e^{-\beta_h t} \int_0^t \left(B_h(u) + B_s C_s(u) + B_m C_m(u) \right) e^{\beta_h u} du$$

which, on substitution of the form for $B_h(u)$, $C_s(u)$, $C_m(u)$ and the constants yields an approximate solution (see Appendix A)

$$C_h(t) = 9.24 \times 10^{-19} t^{3.5} e^{-0.015t}, \qquad (4-7)$$

Again, the total input $Q_{in} = \int_0^{44} B_h(t)dt + B_s \int_0^{44} C_s(t)dt + B_m \int_0^{44} C_m(t)dt$

$$= .0305 \int_0^{44} t^{3.5} dt + 1.93 \times 10^{15} \int_0^{44} C_s(t)dt + 1.02 \times 10^{15} \int_0^{44} C_m(t)dt$$

$$= 1.689 \times 10^5 + 1.29 \times 10^5 + 8.19 \times 10^5 = \underline{1.896 \times 10^5} \text{ lbs}$$

Losses $= (Ab)_h + Q_h + R_h \int_0^{44} C_h(t)dt = \underline{6.84 \times 10^5}$ lbs

and stored material $= (Q + QR)_h C_h(44) = \underline{7.64 \times 10^5}$ lbs.

Input 1.896×10^5 lbs, accounted for 1.44×10^5 lbs.

4.5 Lake Erie

Since Lake Erie has input from Lake Huron as well as from non-point sources, the solution for $C_e(t)$ takes the form

$$C_e(t) = \frac{1}{(Q + \Omega\eta)_e} e^{-\beta_e(t)} \int_0^t \left\{ B_e(u) + B_h C_h(u) \right\} e^{\beta_e(u)} du$$

which, on substitution of the appropriate forms and values becomes

$$C_e(t) = 8.40 \times 10^{-16} e^{-0.0175t} \int_0^t \left\{ .0117 u^{1.5} + (4.45 \times 10^{13})(8.24 \times 10^{-19}) u^{1.5} e^{-1.5u} \right\} e^{.0175t} \quad , \quad (4\text{-}8)$$

which, on integration yields the approximate form

$$C_e(t) = 3.69 \times 10^{-14} t^{1.5} e^{-0.0175t} \left\{ 1 + 0.0303 t e^{-1.5t} \right\} \quad , \quad (4\text{-}9)$$

Now, the total PCB input to Lake Erie from 1930-1974 was

$$Q_{in} + \int_0^{44} B_e(t)dt + B_h \int_0^{44} C_h(t)dt = \underline{1.0196 \times 10^4} \text{ lbs}$$

losses $Q_L = (AD_0 + \delta + R) \int_0^{44} C_e(t)dt = \underline{9.08 \times 10^3}$ lbs

while the stored PCB $= (Q + \Omega\eta) C_e(44) = \underline{7.06 \times 10^3}$ lbs:

Total input $= \underline{1.0196 \times 10^4}$ lbs

Total accounted for $= \underline{9.79 \times 10^3}$ lbs

4.6 Lake Ontario

Again, this lake has input from Lake Erie as well as from non-point sources, hence the solution for $C_O(t)$ takes the form

$$C_O(t) = \frac{1}{(Q + \theta V)_O} e^{-\beta_O t} \int_0^t \left\{ R_O(u) + \beta_E C_E(u) \right\} e^{\beta_O u} du,$$

which has the solution

$$C_O(t) = 7.4 \times 10^{-15} t^{3.15} e^{-0.0215 t}. \qquad (4\text{-}9)$$

The cumulative input to Lake Ontario (up to 1974) is given by

$$Q_{in} = \int_0^{44} R_O(t)\,dt + \beta_E \int_0^{44} C_E(t)\,dt = 6.91 \times 10^5 + 3.37 \times 10^5 = \underline{1.03 \times 10^6} \text{ lbs.}$$

The stored material in 1974 was

$$(Q + \theta V) C_O(44) = \underline{4.26 \times 10^5} \text{ lbs}$$

and the cumulative losses were

$$(AD_O + R + S) \int_0^{44} C_O(t)\,dt = \underline{5.96 \times 10^5} \text{ lbs.}$$

Accounted for = $\underline{1.022 \times 10^6}$ lbs

Input = $\underline{1.03 \times 10^6}$ lbs

4.7 Summary

To summarize the results of the previous calculations, for the assumed situation that the only PCB input to the Great Lakes has arisen from fallout,

$$C_s(t) = 2.93 \times 10^{-19} t^{5.5} e^{-0.035t} \quad (4\text{-}5)$$

$$C_m(t) = 5.64 \times 10^{-19} t^{5.5} e^{-0.09t} \quad (4\text{-}6)$$

$$C_h(t) = 8.24 \times 10^{-19} t^{5.5} e^{-0.01t} \quad (4\text{-}7)$$

$$C_e(t) = 3.69 \times 10^{-18} t^{5.5} e^{-0.07t} \quad (4\text{-}8)$$

$$C_o(t) = 7.45 \times 10^{-19} t^{5.5} e^{-0.01t} \quad (4\text{-}9)$$

The results, in terms of estimated concentrations for the lakes, are given in Table 4.7-1

TABLE 4.7-1

Estimated PCB Concentration for the Great Lakes
(in PPT)

Lake	1930	1940	1950	1960	1970	1975
Superior	0	0.09	0.2	1.2	4.1	6.9
Michigan	0	0.16	0.34	1.9	6.4	10.3
Huron	0	0.22	0.41	2.13	6.5	10.0
Erie	0	0.70	0.86	2.79	5.11	6.1
Ontario	0	0.21	0.41	2.24	7.17	11.4

4.8 Effect of Point Source Inputs

It is not reasonable to assume that the only input to the lakes is from fallout, when in fact there is reason to believe that, especially for Erie and Ontario, there has been considerable point source input.[19] The concentration as a function of time for these latter lakes can be written in parametric form, where (the coefficient α_E or α_O is taken to represent the constant part of the input function, the time dependence is assumed to be the same for fallout as for point sources),

$$B_E(t) = \alpha_E t^{1.5}$$

$$B_O(t) = \alpha_O t^{1.5}$$

then

$$C_E(t) = 3.18 \times 10^{-15} t^{1.5} e^{-0.015t} \alpha_E \left\{ 1 + \frac{3.55 \times 10^{-5}}{\alpha_E} te^{-0.015t} \right\} \qquad (4\text{-}10)$$

and

$$C_O(t) = 5.96 \times 10^{-17} t^{1.5} e^{-0.015t} \alpha_O \ , \qquad (4\text{-}11)$$

Now, to investigate the effects of point sources, the concentration $C_E(t)$ and $C_O(t)$ are calculated assuming that point source contributions are, in terms of the fallout contribution, 20%, 40%, 75%, 100% and 200% respectively. The appropriate value of α_E and α_O are given below in Table 4.8-1 which also contains the respective concentration $C_E(45)$ and $C_O(45)$ as well as $C_E(42)$ and $C_O(42)$. (45 = 1975; 42 = 1972)

The estimated concentrations in Lake Ontario for 1972 as displayed in Table 4.8-1 are to be compared with the measured values taken by C. L. Haile et al[20] which show aqueous concentration ranging from 35 ppt to a high of 97 ppt in the summer of 1972.

[a]Note that throughout, the "aqueous concentration" that is computed is not corrected for suspended matter. There is some question of the Haile data in that the samples were probably not adequately filtered and therefore represent $C_W(t)$ rather than $C_W'(t)$ - see Section 3.5 for a further discussion.

Table 4.8-1

Effect of Point Sources on Lake Erie and Lake Ontario
Estimated Aqueous Concentrations of PCBs

Percent Point Source	q_E	C_E(42) (ppt)	C_E(45) (ppt)	q_O	C_O(41) (ppt)	C_O(45) (ppt)
0	.0117	5.94	6.1	.0125	8.70	11.4
20	.014	6.03	6.78	.015	10.4	14.4
40	.0164	6.82	7.49	.0175	12.2	16.8
75	.0205	7.93	8.70	.0219	15.2	21.0
100	.0234	8.72	9.52	.025	17.4	24
200	.0351	11.91	13.0	.0375	26.1	36

4.9 Comparison of Derived Results with Experimental Data

In a recent extensive review of the PCB contamination of the Great Lakes and their tributaries by the Canadian Environmental Contaminants Committee[21] there are presented estimates of the PCB inputs to the four Canadian lakes as well as some estimates of the average sediment PCB concentrations and estimated total sediment PCB loads. Although these data are somewhat fragmentary and derived from the immediate past, it is possible to compare the estimates to those derived from the model. Table 4.9-1 is derived partially from Table 28[21] and from the results of Section 4 of this study.

TABLE 4.9-1

Estimated PCB Load in the Sediments of the Great Lakes

	CANADIAN ESTIMATES[21]		MODEL ESTIMATES*	
Lake	Average Sediment Concentration (ppb)	Load (lbs)	Average Sediment Concentration (ppb)	Load (lbs)
Ontario	103	6.6×10^5	13.4	8×10^5
Erie	100	4×10^4	9	9×10^3
Huron	4.25	3.5×10^4	8	7×10^4
Superior	30	7.9×10^4	6.4	3.7×10^4

*From Equations (4-5) through (4-9) and the data in Table 4-1.

In the discussion that precedes the presentation of Table 28[21] it is pointed out that the data from which the average concentration of PCBs within the various sediments are not complete and thus the estimates of average concentration may well be considerably in error, probably on the high side. In addition, the existence of marked variations in sediment thickness and the extreme variations in PCB concentrations found in Lake Erie[21] make an estimate of average concentration and PCB load very difficult. The comparison demonstrated in Table 4.9-1 is further confused since the estimates of sediment concentration derived from the normal [Equations (4-5) through (4-9)] are based on fallout as the only source of PCB to the lakes; an assumption that is surely not correct. If point sources

are included as is discussed in Section 4.8, the average water concentration derived from the model is increased and so is the PCB concentration within the sediments.

If it is assumed that the average sediment concentration on Lake Superior was as high as 30 ppb in 1974, then the corresponding average water concentration over the interval 1930-1974 would have been

$$\bar{C}_s = \frac{\bar{C}_{sed}}{\beta} = 7.13 \times 10^{-13} \quad ,$$

But, in general

$$C_s(t) = a_s t^{3.3} \quad ,$$

and

$$\bar{C}_s(t) = \frac{a_s}{44}\int_0^{44} u^{3.3}du = 7.13 \times 10^{-13}$$

Hence

$$C_s(t) = 1.58 \times 10^{-15} t^{3.3} \qquad (4\text{-}12)$$

Evaluation of Equation (4-12) for 1974 (t = 44) yields

$$C_s(44) = 38.7 \text{ ppt} \quad ,$$

With an aqueous PCB concentration as high as 38 ppt, it could logically be assumed that the higher predittators could easily exhibit PCB concentrations in the range of hundreds of parts per million.

Thus, it would seem that the Canadian[21] estimate of the sediment PCB loads for the Great Lakes is probably high.

4.9.1 Fallout on Lake Erie and Ontario

In the Canadian report[21] it is suggested that the atmospherically derived input to Lake Erie and to Lake Ontario was of the order of 10^3 kg/yr = 2.2×10^3 lbs/yr.

From the assumed fallout rate of 1.023×10^{-4} lbs/ft^2/yr, the input to the individual lakes as derived from the model was

$$\text{Fallout input to Lake Erie} = 2.8 \times 10^7 \text{ lbs}$$
$$\text{Fallout input to Lake Ontario} = 2.13 \times 10^7 \text{ lbs},$$

values that are very close to those estimates quoted above, thus the assumption of $a(t) = 50\ \mu g/m^2/yr = 1.023 \times 10^{-4}$ lbs/ft^2/yr for the Great Lakes region seems to be in agreement with other estimates.

If it is now assumed that the fallout rate was essentially uniform over the Lakes region, as in Section 4.1, then the fallout during 1974 onto Lake Superior was of the order of

$$\Delta Q \text{ input} = 3 \times 10^5 \text{ lbs}.$$

On the other hand, returning to Equation (4-12), the aqueous PCB concentration in 1973 and 1974 were

$$C\ (1974) = 39.3 \times 10^{-12}$$
$$C\ (1973) = 35.4 \times 10^{-12} \quad ,$$

hence

$$\Delta Q_{stored} = (Q + Qn)\ \Delta C = 1.08 \times 10^5 \text{ lbs},$$

while

$$\Delta Q_{losses} = (R + AD_0 + S)\ \bar{C} = 2.14 \times 10^5 \text{ lbs}.$$

It is clear that $\Delta Q_{stored} + \Delta Q_{losses} > \Delta Q$ input, from which there are two conclusions; either

(a) There were very large point source inputs of PCBs to Lake Superior during 1974,

or (b) The estimated[31] average PCB concentration of the sediments in Lake Superior are too high.

4.10 Effect of Gradient in B(t)

A major assumption implicit in the treatment of the entire Great Lakes system lies in the assertion that the fallout is essentially the same over Lake Superior as over Lake Ontario. In light of the absence of data to the contrary, there seems to be adequate justification for this simplification. When data are available that allow an estimate of the spatial as well as the temporal variation in fallout, the present model can easily be modified to deal with the more accurate information.

4.11 Effect of Regulatory Actions

As can be seen above, the effect of point source discharges (assumed to be all sources other than fallout) is to sharply increase the concentration in Lake Erie and Lake Ontario. It is assumed that the actual situation in both these bodies involves considerably more input than simply that due to fallout, so that the data in Table 4.7-1 seems to represent the best possible situation, one that would be expected to arise as a result of complete elimination of all non-fallout sources of PCBs.

5.0 CO-DISTILLATION AND THE EVAPORATION MASS CONSTANT K

Solutions that involve poorly soluble solutes usually exhibit properties which differ significantly from predictions based strictly on the mole fractions of the components. Recent work by MacKay and Wolkoff[7] has suggested the type of correction required to deal with surface evaporation of the solute from such a solution. Their principal result[7] is

$$\frac{dM_1}{dt} = -\frac{EP_{1s}M_1}{RT\rho_w V' C_{1s}} C_1 \qquad (5\text{-}1)$$

where, applied specifically to Lake Michigan, the parameters are

- E = mass evaporation rate of water (8.36×10^{11} lb/yr)
- P_{1s} = equilibrium vapor pressure of pure solute
- M_1 = molecular weight of solute (335-Aroclor 1251)
- V' = mass of water from which evaporation occurs
- M_w = molecular weight of water (18)
- C_{1s} = saturation concentration of solute
- P_w = equilibrium vapor pressure water (23.7 mm Hg)
- C_1 = concentration of solute in the evaporation layer
- P_{1s} = effective vapor pressure of solute in solution

Comparison of Equation (5-1) with the definition of K from Equation (1-6) makes clear that, to the degree that Equation (5-1) applies,

$$K = \frac{EP'_{1s}M_1}{RT\rho_w V' C_{1s}} \qquad (5\text{-}2)$$

In order to estimate K from (5-2) it is necessary to determine the vapor pressure of the PCBs.

5.1 Vapor Pressure of the Aroclors

Data published by Hamamto[22] giving the vapor pressure of the several Aroclor mixtures over the temperature range 150-300°C may conveniently be extended to cover the lower temperature ranges by using the general relationship[23]

$$\log(VP) = \alpha - \frac{\beta}{T} \qquad (5\text{-}1)$$

where VP is in mm Hg, and T is the absolute temperature. By standard regression analysis (Appendix A), the appropriate values of α and β were computed as displayed in Table 5.1-1. In addition, the vapor pressure at 760 mm Hg occurs at the normal boiling point, so that a check of the validity of the extrapolation may be made by comparing the estimated boiling temperature in Column 5 with the published value[24] of the boiling range in Column 6.

Table 5.1-1
Vapor Pressure Parameters for Aroclor Mixtures

Aroclor	CIF	α	β	T_{boil} (Est.)	Boiling Range
1242	3.65	20.496	8.088×10^3	311°C	325-366°C
1248	4.32	19.448	7.793×10^3	335°C	340-375°C
1254	5.34	20.36	8.537×10^3	349°C	365-390°C
1260	6.48	19.557	8.445×10^3	380°C	385-420°C

The actual vapor pressure curves, as reported by Hamamto[22] are plotted in Figure 5.1-1 with the extension to lower temperatures, using the parameters in Table 5.1-1 in Equation (5-2), plotted in Figure 5.1-2.

If the PCBs in solution in the water are assumed to be Aroclor 1254, the vapor pressure, at ambient temperature 20°C, should be

$$(VP)_{20°C} = 1.5 \times 10^{-4} \text{ mm Hg}$$

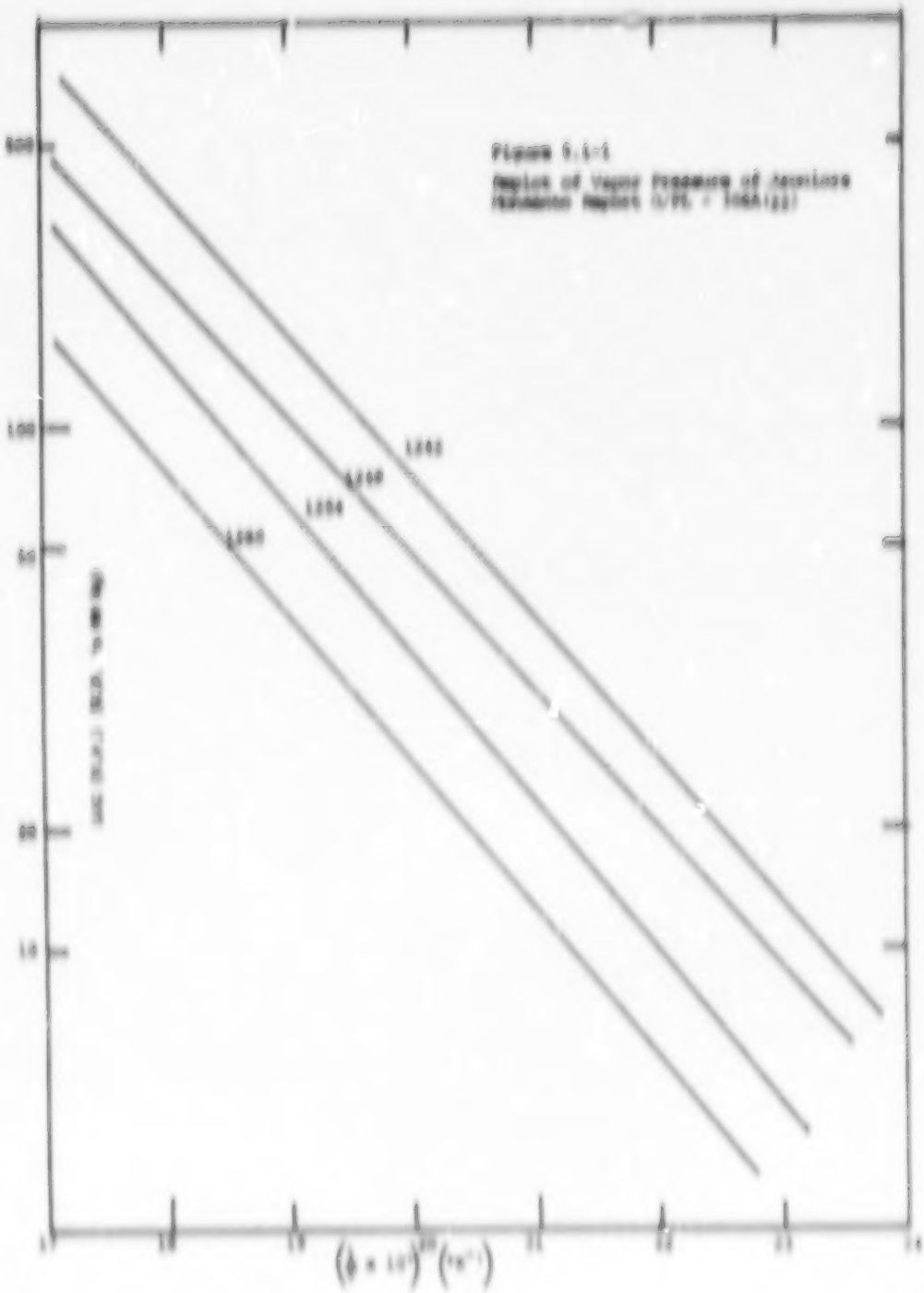


Figure 5.1-1
Region of vapor pressure of zeolites

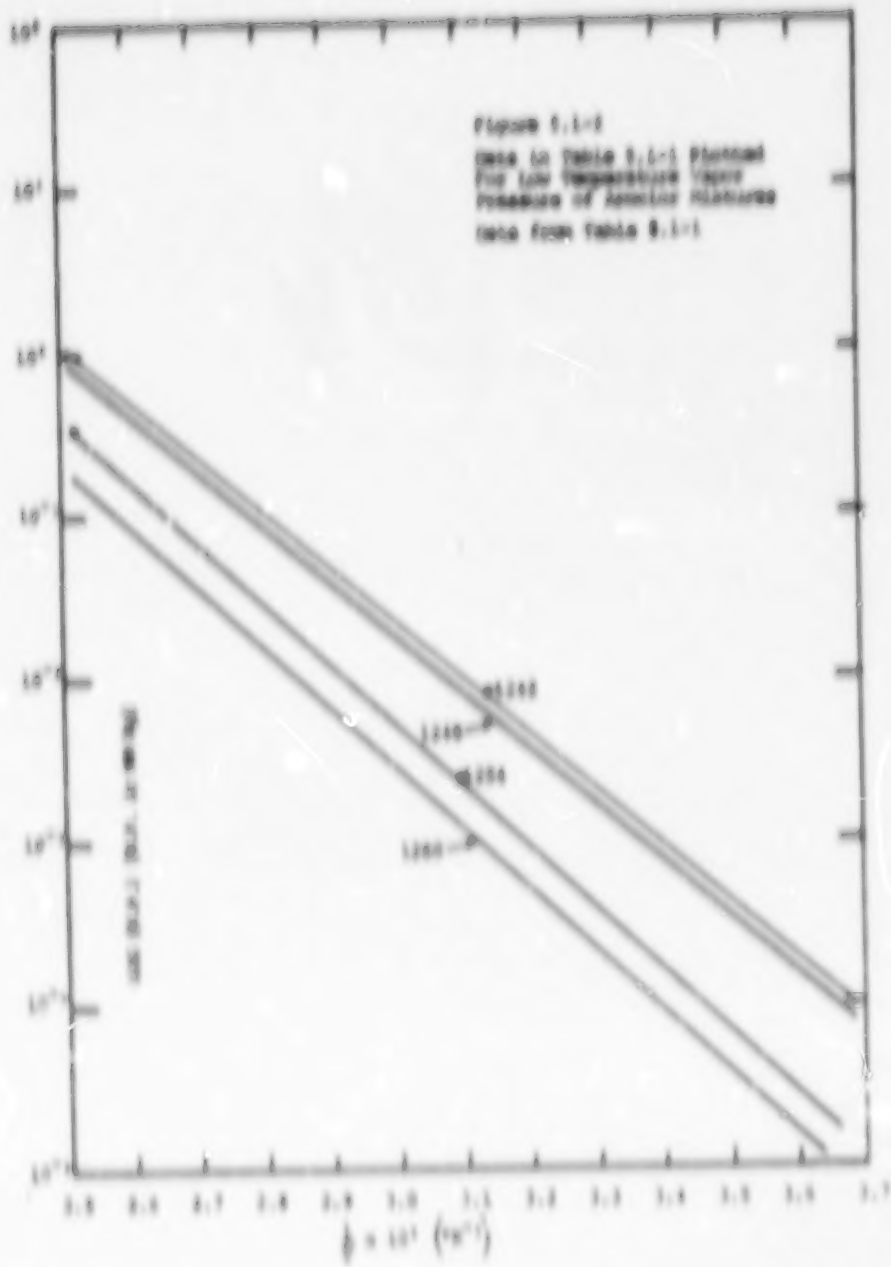


Figure 5.1-1
Data in Table 5.1-1 Plotted
For Low Temperature Vapor
Pressure of Atomic Mixtures
Data from Table 5.1-1

5.1.3 Self Evaporation Rates for Aroclor 1254

In order to verify the validity of the computed vapor pressures displayed in Figure 5.1-2 it is appropriate to examine the published data on the evaporation rate of Aroclor 1254 from a free surface of the pure material. Hansen[25] has published evaporation data at 60°C and 100°C while Haque *et al*[26] have studied self evaporation at 25°C with the results tabulated in Table 5.1.3-1.

Table 5.1.3-1

Self Evaporation Rates Aroclor 1254

T(°C)	dw/dt (gm/cm²/sec)
25°	3.315×10^{-11}
60°	9.95×10^{-10}
100°	1.47×10^{-8}

In order to extend these data to temperatures other than those at which measurements have been made, it is appropriate to have recourse to the kinetic theory of evaporation[27] which supposes that the rate of condensation of a gas of molecular weight M, at an absolute temperature T and a vapor pressure P is given as

$$\frac{dw}{dt} = \alpha \sqrt{\frac{M}{2\pi RT}} P \quad \left(\frac{gm}{cm^2 sec}\right) \tag{5-4}$$

where

R = universal gas constant = 8.317×10^7 ergs/°K/mole
M = molecular weight in gm/mole
T = absolute temperature in °K
P = vapor pressure at temperature T in dynes/cm²

The factor α expresses the probability that the colliding molecule will stick to the surface rather than simply rebound; clearly $\alpha \leq 1$. The relevance of Equation (5.4) to the problem of evaporation derives from the fact that, at equilibrium in a closed system, the rate of condensation of molecules on the

surface must exactly equal the rate at which they leave the surface. Thus, if the system were rearranged so that the evaporated molecules were completely removed while all other parameters were kept constant, then the rate of evaporation would be given by Equation (5-4).[28]

Interchanging the measured evaporation rates from Table 5.1.2-1 into Equation (5-4) results in the computed values of α as shown in Table 5.1.2-2.

Table 5.1.2-2
α Values for Aroclor 1254 (Equation 5-4)

26°C	$\alpha = 0.905$
60°C	$\alpha = 0.907$
100°C	$\alpha = 0.905$

The consistency of the computed α values, as shown in Table 5.1.2-2 may be taken as evidence of the excellent precision of the measured values[25,26] and also of the validity of the extrapolated vapor pressure curves shown in Figure 5.1-2.

The specific measured as well as several computed $\frac{\partial m}{\partial t}$ values for Aroclor 1254 are plotted in Figure 5.1.2-1.

5.2 Calculation of the Evaporation Coefficient K for Lake Michigan

5.2.1 Mass Balance at Lake Surface

In Section 3.2, the detailed balance of PCBs within the lake in 1975 was computed. If the results are particularized into fluxes in $gm/cm^2/sec$, the effects at the surface may be summarized as follows:

Fallout	1.59×10^{-13} $gm/cm^2/sec$
Evaporation	6.34×10^{-17} $gm/cm^2/sec$
Net PCB input	9.51×10^{-17} $gm/cm^2/sec$

Simultaneously

Net Water Evaporated	3.13×10^{-4} $gm/cm^2/sec$

Now, from the above, the PCB concentration in the vapor state (ratio of PCB evaporation flux to the water evaporation flux)

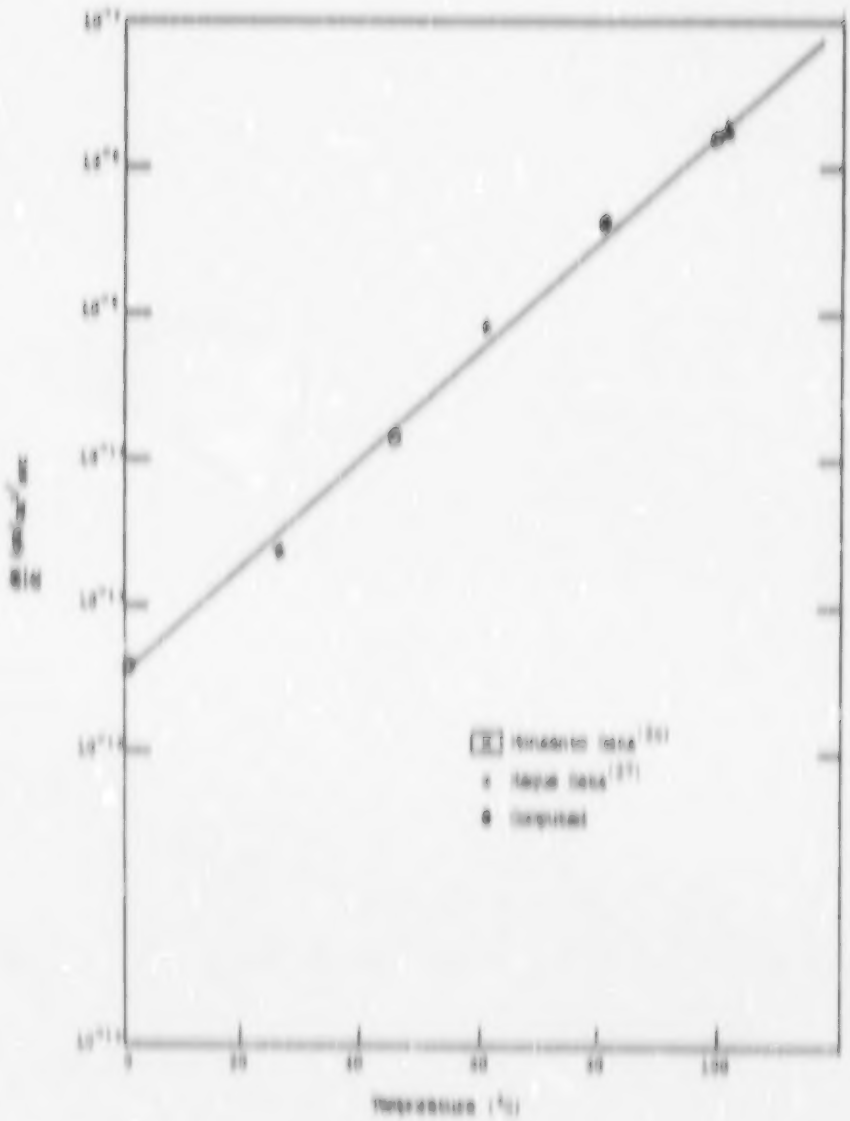


Figure 5.1.2-1
Mass Evaporation Rate Arrelor 1254
From Itself

$$C_{vap} = \frac{6.34 \times 10^{-17}}{2.13 \times 10^{-6}} = 2.98 \times 10^{-11} \quad (1975) \qquad (5\text{-}5)$$

The concentration shown in Equation (5-5) is clearly not to be interpreted as the ambient air concentration over the lake, only as one component thereof; there is also the airborne load which is the origin of the fallout.

It is tentatively assumed that the surface (aqueous) concentration is equivalent to the vapor concentration, and further, from Equation (3-2), the bulk aqueous concentration was 8.5×10^{-12} (in 1974), then

$$C_s = C_{vap},$$

$$\text{and,} \quad C_s = \gamma C_w$$

$$\text{where} \quad \gamma = \frac{2.98 \times 10^{-11}}{8.5 \times 10^{-12}} = 3.4 \qquad (5\text{-}6)$$

Then, using the computed value of C_Δ and γ, it can be shown that (from Equations (3-2) and (5-6)

$$\frac{\Delta C_\Delta}{\Delta t} \text{ (1974-1975)} = 3 \times 10^{-12} \text{ yr}^{-1}$$

or,

$$\left(\frac{\Delta C_\Delta}{\Delta t}\right) \text{sec}^{-1} = 9.68 \times 10^{-19} \text{ sec}^{-1}$$

Thus, the total gain in the "dissolved" PCB within the surface layer of thickness ζ was

$$(\Delta M)_{\text{layer}} = 9.68 \times 10^{-19} \zeta \text{ gm/sec/cm}^2, \qquad (5\text{-}7)$$

On the other hand, a layer of thickness ζ with a concentration gradient

$$\frac{\Delta C}{\zeta} = \frac{C_s - C_w}{\zeta}$$

will experience a diffusion current[29] given by

$$\left(\frac{\Delta m}{\Delta t}\right)_{diffusion} = D\,\frac{\Delta C}{\zeta} \qquad (5\text{-}8)$$

where the cross-sectional area is taken as 1 cm^2, D in $\frac{cm^2}{sec}$ and ΔC is gm/cm^3. (Note, most of the concentrations used in this paper have been in terms of gm/gm, i.e., dimensionless.)

Introducing the concentrations and thus the concentration gradient, and taking D to be of the order of 10^{-5} cm^2/sec, which is the usual magnitude for organic solutes in water[30]

$$\frac{\Delta m}{\Delta t}_{diff} = \frac{2 \times 10^{-16}}{\zeta} \qquad (5\text{-}9)$$

If the sum of Equation (5-7) and (5-8) is equated to the net PCB gain in 1975, the resulting equation may be solved for ζ

$$9.68 \times 10^{-11}\,\zeta + \frac{2 \times 10^{-16}}{\zeta} = 9.51 \times 10^{-17} \qquad (5\text{-}10)$$

$$\zeta^2 - 9.82 \times 10^{-7}\,\zeta + 2.066 \times 10^{-6} = 0$$

from which,

$$\zeta = 2.2 \text{ cm (or 980 cm)} \quad , \qquad (5\text{-}11)$$

Since the layer of enhanced surface concentration is usually assumed to be very thin,[31] the value $\zeta = 2.2$ cm is selected in what follows:

From Equation (5-7), the net gain during 1975 of the solute load within the layer was

$$\left(\frac{\Delta M}{\Delta t}\right)_{layer} = 2.13 \times 10^{-19} \text{ gm/cm}^2/\text{sec} \qquad (5\text{-}12)$$

Correspondingly, the loss from the layer due to diffusion into the bulk water was

$$\left(\frac{\Delta M}{\Delta t}\right)_{\text{diffusion}} = 9.1 \times 10^{-17} \text{ gm/cm}^2\text{/sec} \qquad (5\text{-}13)$$

And the sum of these are

$$\left(\frac{\Delta M}{\Delta t}\right) = 9.12 \times 10^{-17} \text{ gm/cm}^2\text{/sec}$$

which compares to the net loss to the surface and bulk of 9.51×10^{-17} gm/cm^2/sec. Further, from Equation (5-13) it is seen that a total of

$$\left(\frac{\Delta M}{\Delta t}\right)_{\text{bulk}} = 3840 \text{ lbs/yr}$$

entered the lake during 1975 from the diffusion of fallout material through the surface layer.

5.2.2 Effective Surface Vapor Pressure/Ultimate Solubility Ratio

If Equation (5-1) is now used to compute the rate of effective vapor pressure to solubility limit, using Equation (5-1),

$$\left(\frac{P_{is}}{C_{is}}\right)_{\text{eff.}} = \left(\frac{\Delta m}{\Delta t}\right)_{\text{evap}} \frac{18\, P_M}{RT_1 C_1} = 1.26, \qquad (5\text{-}14)$$

On the other hand, for the "pure" Aroclor 1254,(32)

$$\left(\frac{P_{is}}{C_{is}}\right)_{\text{pure}} = 2.33 \times 10^{1} \qquad (5\text{-}15)$$

The physical meaning of the result shown in Equation (5-14) is not clear but it can certainly be stated that both the effective vapor pressure and the effective limiting solubility within the surface layer are higher than the corresponding values for the bulk solution.

It is true that the ratio $\left(\frac{p_{is}}{C_{is}}\right)_{pure}$ is used by MacKay and Wolkoff[7] as a measure of the activity of the PCB in solution in water; hence, one should perhaps consider the ratio in Equation (5-14) as a measure of the activity of PCB within the surface layer. If this is true, then it should be possible to demonstrate that a layer of enhanced concentration is, in fact formed by these differences in activity within the bulk solution and within the layer. In this case, the equilibrium concentration within the layer would arise as a consequence of the combined effect of an activity gradient enhancing the layer concentration while ordinary concentration dependent diffusion plus surface evaporation would tend to decrease the layer concentration. This point merits further detailed consideration.

5.3 Evaporation Rate Constant K

In view of the uncertainty in the determination of $\left(\frac{p_{is}}{C_{is}}\right)$ within the surface layer, it is clear that the determination of K from Equation (5-2) is not possible. Thus, K, the surface evaporation rate constant must remain as an empirical parameter to be determined by an iterative processes such as is used in Section 3.

When applied to other lakes, the corrected evaporation rate constant is determined by

$$\left(\frac{K}{K'}\right)_L = \left(\frac{K}{K'}\right)_{Mich} \qquad (5\text{-}10)$$

as has been done in deriving the data in Table 4-1.

5.4 Comparison With Experiment

Bidleman and Olney[33] reported a series of measurements of PCB concentrations within the surface layer (150 microns) and in the corresponding subsurface regimen. Their Table 2[33] is partially reproduced below:

Table 5.4-1

Bidleman and Olney Surface Concentration Data[44]

Site #2	C_{SL} ($\times 10^{15}$)	C_{bulk} ($\times 10^{15}$)	C_{SL}/C_{bulk}
1	11.2	3.6	3.1
2	4.9	<0.9	5.4
3	8.3	1.0	8.3
4	3.8	<0.9	4.2
5	5.6	1.6	3.5
6	5.0	1.8	2.8
7	8.4	<0.9	9.3

From which $\frac{C_{SL}}{C_{bulk}} = \gamma = 5.2$

It is recognized that the measurements cited in Table 5.4-1[33] were made in sea water where it is to be expected that C_{ls} will be less than for fresh water due to the competitive effects of the solvated ions with the poorly soluble PCB molecules.[34] This reduction in C_{ls} can only result in an increase in the tendency to retain PCBs on the surface. In this case one would anticipate that the ratio of surface layer concentration to bulk concentration might well exceed that for the case of fresh water systems.

A comparison of the Bidleman and Olney[33] results with those derived in the discussion leading to Equation (6-5) suggests that the assumption that the PCB concentration in the evaporated material (water plus PCB) is not very different from that found in the uppermost boundary is realistic. It should also be noted that the situation in Lake Michigan differs from that treated by MacKay and Wolkoff[7] in that the latter discussion dealt with the situation wherein the only source of solute was that initially present in the solution; whereas the case treated here has the additional complication due to the fallout input.

6.0 AN ESTIMATE OF THE PCB CONCENTRATION IN A TYPICAL LAKE TROUT WHEN EXPOSED TO AN AQUEOUS PCB CONCENTRATION

6.1 Development of the Model

Consider a fish with PCB intakes and outputs as represented schematically

FIGURE 6.1-1. SCHEMATIC FISH

Where: $F_I(t)$ = PCB intake due to the inclusion in food per unit fish mass
$F_O(t)$ = PCB output contained in food wastes per unit fish mass
$R_I(t)$ = PCB intake with respiratory intake water per unit fish mass
$R_O(t)$ = PCB output with respired water per unit fish mass
$M(t)$ = PCB output by lipid turnover, metabolism or other clearance routes per unit fish mass
$C_{fe}(t)$ = PCB concentration in the edible portion of the fish
$C_w(t)$ = PCB concentration in fishes' aqueous environment.

Now, the mass balance implied by Figure 6.1-1 may be summarized by the equation, in the limit $\Delta t \to 0$,

$$\frac{dC_f(t)}{dt} = F_I(t) - F_O(t) + R_I(t) - R_O(t) - M(t)$$

$$\frac{dC_f(t)}{dt} = \Delta F_I(t) + \Delta R_I(t) - M(t) \quad , \qquad (6\text{-}1)$$

In order to simplify Equation (6-1),

let
$$\left.\begin{aligned} \Delta F(t) &= k_f C_w(t) \\ \Delta R(t) &= k_r C_w(t) \\ M(t) &= k_e C_f(t) \end{aligned}\right\} \qquad (6\text{-}2)$$

and $k_e = k_f + k_r$

With these substitutions, Equation (6.1) takes the form

$$\frac{dC_f(t)}{dt} + k_2 C_f(t) = k_1 C_w(t) \quad . \tag{6-3}$$

In order to solve Equation (6-3) multiply both sides of the equation by exp $(k_2 t)$ to yield

$$\frac{d}{dt}\left[C_f(t) \exp (k_2 t)\right] = k_1 C_w(t) \exp (k_2 t)$$

for which the solution is

$$C_f(t_2) \exp (k_2 t_2) - C_f(t_1) \exp (k_2 t_1) = k_1 \int_{t_1}^{t_2} C_w(u) \exp (k_2 u) du, \tag{6-4}$$

where u has been introduced as an integrating variable.

The general solution of Equation (6-1) is given as

$$C_f(t_2) = k_1 e^{-k_2 t_2} \int_{t_1}^{t_2} C_w(u) e^{k_2 u} du + C_f(t_1) e^{-k_2 (t_2 - t_1)} \quad . \tag{6-5}$$

If it is asserted that the average age of consumable fish is τ, then the limits of integration in Equation (6-5) become $t - \tau$ and t. With the additional assumption that

$C_f(t - \tau) = 0$, Equation (6-5) becomes

$$C_f(t) = k_1 e^{-k_2 t} \int_{t-\tau}^{t} C_w(u) e^{k_2 u} du + k_3 e^{-k_2 t} \quad . \tag{6-6}$$

Now, following the definition of parameters k_1 and k_2 (from Equation (6-3)), the ratio $C_f(t)/C_w(t)$ will approximate the bioconcentration factor as $t \to \infty$. Stated more precisely, for any $C_w(t) = rt^n$ where n is an integer ≥ 0,

$$\lim_{t \to \infty} \frac{C_f(t)}{C_w(t)} = \frac{k_4}{k_2} (1 - e^{-(k_2)}) = \frac{k_4}{k_2} \qquad (6\text{-}7)$$

since $e^{-t/k_2} \ll 1$ in the limit.

6.2 Determination of the Rate Constants k_1 and k_4

The difficulty in application of Equation (6-6) lies in the selection of appropriate values for k_1 and k_2 which relate respectively to PCB uptake and clearance rate constants, as can be seen from Equation (6-3). Experiments by Branson et. al.[35] have determined these constants, for lake trout, to be

$$\left.\begin{aligned} k_1 &= 1.04 \times 10^3 \ yr^{-1} \\ k_2 &= 10.95 \ yr^{-1} \end{aligned}\right\} \qquad (6\text{-}8)$$

The procedures used to determine these values[36] involved only a PCB-contaminated aqueous environment and a non-contaminated food system. Hence the k_1 value cited in Equation (6-8) is actually the $k_{1\beta}$ in Equations (6-2) and therefore reflects a minimum value of k_1. In point of fact, the $k_{1\alpha}$ component of k_1 is likely to be significantly larger than $k_{1\beta}$ since substantial bioaccumulation of PCBs may already have occurred up to the trophic level of the fish diet, particularly for predatory fishes.

If one assumes the Branson[35] value for $k_{1\beta}$ value to be equal to k_1 (i.e., $k_{1\alpha} = 0$), a computation of the C_f (1970), for Lake Michigan yields C_f (1970) = 29 ppb, a value far below the measured values for that era.[37]

Experimental determination of the rate constant $k_{1\alpha}$ would be difficult and does not appear to have been attempted. On the other hand, if the empirical values for Lake Michigan are inserted in Equation (6-5), the result will lead to an empirical estimate of $k_{1\alpha}$ and, using Branson's value of $k_{1\beta}$, to an estimate of k_f as follows. Using the measurements of $C_f(t)$ on age 4 (Salvelinus Namaycush)

by Willford et. al.[38] corrected by the 1:3 ratio of whole fish concentration to muscle concentration as used by Branson et. al.[35] and by Hansen, et. al.[39], and the expression for $C_w(t)$ derived in Section 3 (Equation (3-2)), Equation (6-5) is solved by the method indicated in Appendix A (Section A.5) with the results indicated in Table 6.2-1. From Table 6.2-1, the average value of k_1 is

$$\bar{k}_1 = 4.28 \times 10^4 \text{ yr}^{-1} \qquad (6\text{-}9)$$

Clearly, a comparison of the average k_1 from Equation (6-9), with the value of k_2 given in Equation (6-8), $k_1 >> k_2$ so that, the trout intake from its diet is about 50 times that due to respiration.

Further, a comparison of k_1 and k_2, through Equation (6-7) suggests a bioconcentration factor

$$n = \frac{k_1}{k_2} = 3.9 \times 10^3 \text{ (edible)} - 1.17 \times 10^4 \text{ (whole fish)} \qquad (6\text{-}10)$$

Using Willford's data[40] and the estimated aqueous concentration from Table 3.2-1, the estimated bioconcentration factor,

$$n = 1.33 \times 10^4 \ .$$

Further, Veith[41] reports maximum concentration factors for the trout to be of the order of 1.5×10^4.

6.3 Effect of Regulatory Actions on Trout PCB Concentrations

The differential equation, Equation (6-5), particularized for trout becomes

$$C_f(t) = 4.28 \times 10^4 e^{-(10.0+k)t} \int_{-\tau}^{t} e^{(10.0+k)u} C_w(u)\,du + k_2 e^{-(10.0+k)t} \qquad (6\text{-}11)$$

which, following the method outlined in Appendix A (leading to Equation (A-13), may be solved numerically to yield the results given in Figure 6.3-1 for two different values of β, where β is defined in terms of the differential equation

$$\frac{dC_f(t)}{dt} + k_2 C_f(t) = \beta t^{1.5} \ . \qquad (6\text{-}12)$$

TABLE 6.2-1

ESTIMATES OF k_1 (UPTAKE RATE (KBQ/DAY))

Date	$\bar{T}$ (yrs)	U_{fo} $\times 10^{3}$	τ	$C_w(t)$ $\times 10^{11}$	α	β	δ	I_1^* $\times 10^{-4}$	I_2^{**} $\times 10^{2}$	k_1 $\times 10^{-4}$
9/28/72	43.75	4.3	6.38	12.3	468	36.36	398	2.1	0.349	3.55
9/19/73	43.37	6.3	5.93	13.1	479	37.79	414	2.4	7.76	4.61
10/9/74	44.77	7.6	6.08	15.2	490	38.68	424	2.9	1.64	4.67

$$* \quad I_1 = \tau^{\delta+1} \int_0^{\lambda} e^{-\alpha\beta}(1-\beta)^{\delta+1} d\beta$$

$$** \quad I_2 = \beta^{\delta+1} e^{-k_1 \tau} \int_0^{\lambda} e^{-\delta\alpha}(1-\alpha)^{\delta+1} d\alpha$$

Note that the log $[C_f(t)]$ is plotted against the data in Figure 6.3-1.

The plotted curves in Figure 6.3-1 represent the concentration in the edible portion of a trout as a function of time, specifically, for a trout born in 1930. To discern what would happen to an animal born at a later date, the operative differential equation may be written

$$\frac{dC_f(t)}{dt} = k_1 C_w(t) - k_2 C_f(t) \quad . \tag{6-13}$$

If it is assumed that at birth $C_f = 0$, then because of the large value of k_1 and the non-zero value of $C_w(t)$ for $t > 0$ (later than 1/30), the rate of change of $C_f(t)$ is initially very large. Eventually, any given fish, regardless of its time of initial injection into the polluted water, will arrive at the limiting concentration shown in Figure 6.3-1. Clearly, from Equation (6-13) when

$$k_1 C_w(t) = k_2 C_f(t)$$

or

$$\frac{C_f(t)}{C_w(t)} = \frac{k_1}{k_2}$$

then

$$\frac{dC_f(t)}{dt} = 0 \quad .$$

Now, suppose that, at $t = t_0$, $C_w(t_0) = C_w(0)$ and $C_f(t_0) = \frac{k_1}{k_2} C_w(0)$.

Further, suppose that, as a result of regulatory activity, the input of PCBs were to be decreased so that

$$C_w(t > t_0) = C_w(0) e^{-\gamma(t - t_0)} \tag{6-14}$$

Substitution of Equation (6-14) into Equation (6-13) results in the formal solution

$$C_f(t) e^{k_2 t_0} = k_1 C_w(0) e^{\gamma t_0} \int_{t_0}^{t} e^{(k_2 - \gamma) u_{du}} \quad . \tag{6-15}$$

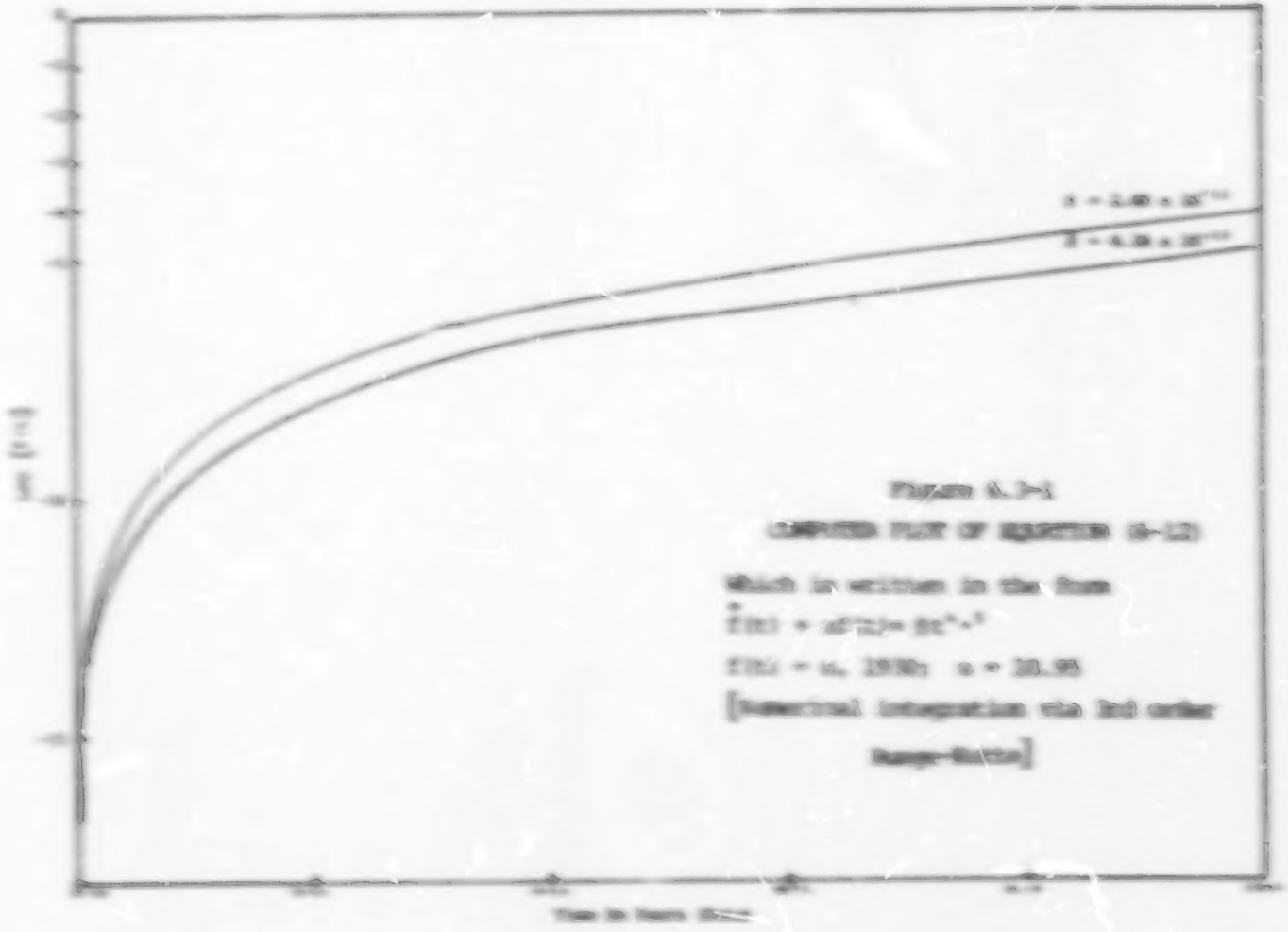


Figure 6.3-1

COMPUTER PLOT OF EQUATION (6-12)

Which is written in the form

$\dot{x}(t) = x^{(n-1)} - kx^{n} - 1$

$f(t) = u_s$ 1938; $a = 20.95$

[Numerical integration via 3rd order Runge-Kutta]

Several cases are obvious:

a) Suppose $\gamma = 0$, i.e. for $T > t_0$, $C_w(T) = C_w(t_0)$

$$e^{k_2 T}\left\{ C_f(T) - \frac{k_1}{k_2} C_w(0) e^{-k_2 (T-t_0)} \right\} = \frac{k_1 C_w(0)}{k_2} e^{k_2 T} \left\{ 1-e^{-k_2 (T-t_0)} \right\}$$

which, on simplification yields

$$C_f(T) = \frac{k_1}{k_2} C_w(0) - C_f(t_0) \qquad (6\text{-}16)$$

as required.

b) Suppose $\gamma \neq 0$ but, since any practical regulatory effort will take a number of years to reduce the PCB concentration to $1/_e$ of its value at t_0, $\gamma << 1$ and hence $\gamma << k_2$; under these circumstances, Equation (6-15) becomes, after integration and simplification,

$$C_f(T) = \frac{k_1}{k_2} C_w(0) e^{-k_2 (T-t_0)} \left[1-e^{-\gamma (T-t_0)} \right] + \frac{k_1}{k_2} C_w(0) e^{-\gamma (T-t_0)} \quad . \qquad (6\text{-}17)$$

Note that, for $T = t_0$, Equation (6-17) reduces to

$$C_f(T) = \frac{k_1}{k_2} C_w(0)$$

and for $T \to \infty$,

$$C_f(T=\infty) = \frac{k_1}{k_2} C_w(0) e^{-\gamma (T-t_0)} \to 0, \qquad (6\text{-}18)$$

Thus, from a comparison of Equation (6-18) with (6-14), it is clear that the rate at which the PCB concentration decreases in the trout is exactly the rate at which the PCB concentration decreases in the aqueous surroundings.

c) Suppose that a trout with PCB concentration $C_f(t_0)$ is suddenly removed from PCB contaminated water and introduced into clean water. Under these circumstances, for $t > t_0$, Equation (6-13) becomes

$$\frac{dC_f(t)}{dt} = - k_2 C_f(t) \quad ,$$

for which the solution is

$$C_p(t > t_0) = C_p(t_0)e^{-k_1(t-t_0)}$$

and the time interval $(t-t_0) = (\Delta t)_{1/2}$ required for a 50 percent reduction in concentration is

$$(\Delta t)_{1/2} = \frac{0.693}{k_1} = \underline{\underline{22 \text{ days}}} \qquad (6\text{-}19)$$

7.0 FURTHER WORK

The results presented in this work have been derived under a number of assumptions which are justified primarily because much of the basic information needed to avoid such assumptions is simply not available. In this category are included such factors as total biotic mass, the average biological partition coefficient, the details of biological uptake and clearance of refractory compounds and the nature of the surface layer at the air-water interface and the driving forces which are responsible for the concentration gradient across the layer. Further, there exists no real historical base of data that could be used to establish bench marks to check the validity of the many extrapolations that have been used.

Other of the assumptions have been introduced for the sake of physical or mathematical simplification. In this category should be included the assumptions that the Aroclors act like a single compound; that there is no degradation of the PCBs in the environment; that it is proper to characterize the sediments by a single partition coefficient and that the fallout areal density is independent of the latitude. This category of assumptions can be removed from the model at the expense of some increase in mathematical complexity. Several examples of the manner in which these assumptions can be removed are given below in schematic form. It would be of considerable practical interest to further explore these avenues.

In addition, the mass balance model, while it has been explicitly applied to the PCB problem, should be capable of extension to the study of other refractory compounds, for example to mirex. It should also be pointed out that this type model presents many points that should lend themselves to direct experimental testing from which more accurate models may be evolved.

The fact that the model is capable of being expressed in the form of continuous functions of time with an explicit functional form for the driving function is of significance in an attempt to ascertain the effect of alternative regulatory actions. The effect of any regulatory activity will be felt in terms of an alteration of the PCB input to the target region. If this alteration can be expressed as a function of time (in a reasonably well-behaved functional form),

the mass balance equation can be integrated to estimate the time scale required to obtain the desired reduction in PCB concentration in any phase of the system. This ability is of prime importance in comparing the effects of several alternative regulatory activities.

The next several sections represent, in schematic form, the methods that may be used to remove one or another of the assumptions that have been introduced for physical or mathematical convenience.

7.1 Introduction of Environmental Degradation

If it is assumed that the species of PCB with chlorine numbers of three (3) or less are degraded by environmental processes, then the forcing function B(t) may be rewritten:

$$B(t) = B_1(t) + B_2(t) \tag{7-1}$$

where $B_1(t)$ refers to the lower, degradable species, and $B_2(t)$ to the higher, non-degradable species of PCBs. As before the functional form of the $B_i(t)$ is taken

$$B_i(t) = a_i t^{\beta_i} \tag{7-2}$$

If it is assumed that the decay of $B_1(t)$ may be expressed by a decay constant λ, then

$$\frac{dB_1(t)}{dt} = \lambda a_1 t^{\beta_1} + a_1 \beta_1 t^{\beta_1 - 1} \tag{7-3}$$

where the second term on the right hand side of Equation (7-3) describes the additional input to the reservoir of the lower species while the first term on the right describes the decay of the material already in the environment. On integration of Equation (7-3)

$$B_1(t) = a_1 t^{\beta_1} \left\{ 1 - \frac{\lambda t}{\beta_1 + 1} \right\} \tag{7-4}$$

So that, the driving function B(t) becomes

$$B(t) = a_1 t^{\beta_1} \left\{ 1 - \frac{\lambda t}{\beta_1 + 1} \right\} + a_2 t^{\beta_2} \tag{7-5}$$

As before β_1 and β_2 are derived from the environmental load model exhibited in Appendix C using data from Appendix D. The parameters α_1 and α_2 are derived from experimental data taken recent times and λ is derived from the known degradation data.

In addition to the required modification in the driving function, the two partition coefficients, ρ and η are, in general, dependent of the molecular structure of the partitioned species. Thus, it is to be expected that both will exhibit quite different values for the lower chlorinated PCB species as compared to the higher chlorinated species.

Further, the surface evaporation rate constant K, which appears to depend on vapor pressure as well as limiting solubility, will be different for the two species of PCBs. Thus, the time constant, δ, will be different for the two species. In terms of the solution of the mass balance equation, it is clear that, since there is no coupling between the two species, there should then be two separate differential equations, one for its lower species, the other for the remaining PCB species.

It remains to be pointed out that the additional complexity of treating each level of chlorine substitution as a separate species could also be introduced. The resulting complexity would hardly be justified.

7.2 Airborne Reservoir and the Generation of a Gradient in Fallout

The assumption that $\sigma(t)$ is constant over a large region such as the Great Lakes may be removed by a procedure similar to the following:

Consider a column of air of uniform density and of height h (h is selected so that the surface pressure due to the weight of gas equals the normal atmospheric pressure) located at a position (x, y) on the surface of a flat earth. Let the area of the base of the column be $(\delta x)(\delta y)$ as shown in Figure 7.2-1. Let the average (constant) air velocity, v, be directed parallel to the x axis and let the PCB concentration of the air entering the column be $C(x,t)$ and that leaving be $C(x(t) + \delta x,t)$. It is explicitly assumed that C is not a function of y.

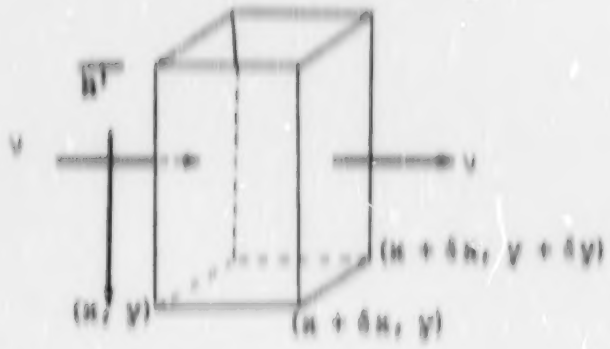


FIGURE 7.2-1
Volume Element for Airborne Reservoir Computation

Then in the time interval Δt, the amount of PCB entering the column is

$$\Delta M_{in} = v(\delta y)h\, C(x,t)\Delta t$$

and that leaving is

$$\Delta M_{out} = v(\delta y)h\, C(x + \delta x,\ t)\Delta t \quad .$$

Thus, the net change per unit time is

$$\frac{\Delta M}{\Delta t} = v(\delta y)h\, C(x,t) - v(\delta y)h\, C(x + \delta x, t)$$

which on multiplying by $\frac{\delta x}{\delta x}$ becomes, in the limit

$$\frac{dM}{dt} = - v(\delta x)(\delta y)h \frac{\partial C(x,t)}{\partial x} \qquad (7\text{-}7)$$

It is further taken that some of the PCBs within the column are removed by fallout with a decay constant λ, then

$$\frac{dM}{dt}_{fallout} = - \lambda M(x,t) = - \lambda(\delta x)(\delta y)h\, C(x,t) \qquad (7\text{-}8)$$

Further, it is taken that there exists a surface distribution of PCBs, described by $\rho(x,t)$ from which a fraction $\alpha(x,t)$ is vaporized in unit time. Hence the contribution to the mass of PCBs within the column is given by

$$\left(\frac{\partial M}{\partial t}_{evap}\right) = \alpha(x,t)\rho(x,t)\,(\delta x)\,(\delta y) \qquad (7\text{-}9)$$

So that the mass balance, obtained by summing Equation (7-7), (7-8) and (7-9) becomes

$$v\,\frac{\partial C(x,t)}{\partial x} + \lambda C(x,t) = \frac{\alpha(x,t)}{\beta}\rho(x,t) \qquad (7\text{-}10)$$

It is appropriate to note that the definition of $\frac{\partial C(x,t)}{\partial x}$ requires

that t be treated as a constant, so that Equation (7-10) may more properly be written as

$$v\,\frac{\partial C(x,t_i)}{\partial x} + \lambda C(x,t_i) = \frac{\alpha(x,t_i)}{\beta}\rho(x,t_i) \qquad (7\text{-}10')$$

With a suitable definition of $\alpha(x,t_i)$ and $\rho(x,t_i)$, Equation (7-10') may be solved to indicate the variation of the airborne concentration of PCBs with position at a fixed time, i.e., the comparison of the results of measurements taken at widely separated locations at the same time. If Equation (7-10') were solved for a number of different t_i then the resulting set of solutions may be used to construct the time dependence of $C(x,t)$ so as to define the entire function. From such an equation, the fallout may be derived as a function of position and time.

7.3 Introduction of Spatial (or Temporal) Variation of Sediment

In Section 3.3, it was shown that even complex contours of spatial variation of sediment rate or sediment partition coefficient could be incorporated into the mass balance equation. The essential simplifying assumption is that of complete mixing of the water column. If it becomes necessary to consider temporal variations in either sediment deposition rate or chemical content, the complexities introduced are considerable for, in this case, the time constant, β, becomes time dependent. The solution of the mass balance equation must then be accomplished

by a series of summations over small time intervals; there is little likelihood that so simple a solution as expressed by Equations (A-8) or (A-9) can be obtained.

7.4 The Surface Layer and Co-Distillation

As is apparent from the discussion in Section 5, the existence of a surface layer of enhanced concentration is not readily understood. It would appear that the origin of this layer is bound up in the very high activity of a solute such as a PCB in water as compared to the activity such a molecule would exhibit at the air-water interface. Thus, it seems that the driving force to produce the enhanced concentration is just the difference in activity in the bulk as compared to that on the surface which, combined with the loss due to evaporation establishes a dynamic equilibrium constant. Since it appears that this process is of great importance to the mass accounting of a body of water and since, this also could be a significant process for the injection of materials into the atmospheric reservoir, it obviously merits more study.

MATHEMATICAL CONSIDERATIONS

A.1.0 GENERAL

The evaluation of definite integrals of the form

$$I = \int_0^t x^\beta e^{\delta x} dx \quad , \tag{A-1}$$

where t is finite, δ may be either positive or negative and β is non-integer, are of considerable interest in the context of this work. It is appropriate to consider both cases with respect to the sign of δ (the case where $\delta = 0$ is, of course, trivial).

A.1.1 $\delta < 0$

By substitution of $w = \delta x$, the integral I may be transformed into

$$I = \frac{1}{\delta^{\beta+1}} \int_0^{\delta t} w^\beta e^{-w} dw \tag{A-2}$$

which is of the form of the incomplete gamma function[1]* and thus cannot be reduced to elementary functions. The general solution of A-2 is then given by[1]

$$I = \frac{1}{\delta^{\beta+1}} \gamma\left[\beta + 1, \delta t\right] = \frac{1}{\delta^{\beta+1}} \sum_{n=0}^{\infty} (-1)^n \frac{(\delta t)^{n+\beta+1}}{n!(n+\beta+1)} \quad . \tag{A-3}$$

The series in Equation (A-3) may be shown to converge since

$$\lim_{n\to\infty} \left(\frac{a_n}{a_{n+1}}\right) = \lim_{n\to\infty} \left[-\frac{\delta t (n+\beta+1)}{(n+1)(n+\beta+2)}\right] = \lim_{n\to\infty} \left(-\frac{\delta t}{1}\right) = 0, \tag{A-4}$$

In addition,

$$\lim_{n\to\infty} \left|\frac{a_n}{a_{n+1}}\right| = 0, \tag{A-4}$$

---

*All references for this Appendix are listed on page A-6

Thus, the series represented by Equation (A-4) is absolutely convergent for all finite t and δ.

A.1.2 $\delta \geq 0$

In the event that δ is non-negative, evaluation of the integral in Equation (A-1) proceeds by the usual expansion of the exponential in the Maclaurin series,[2] integration of the resulting series term by term and subsequent collection to yield

$$I_{\delta \geq 0} = t^{\beta+1} \sum_{n=0}^{\infty} \frac{(\delta t)^n}{n!(n+\beta+1)} \qquad (A\text{-}5)$$

which is also convergent in the limit as $n \to \infty$, since, as before

$$\lim_{n\to\infty} \left| \frac{a_{n+1}}{a_n} \right| \to 0.$$

A.2.0 PARTICULAR APPLICATIONS TO PROBLEMS ENCOUNTERED

Of specific interest in this work are the two integral forms

$$I_1 = e^{\delta t} \int_0^t x^{\beta} e^{-\delta x} dx \qquad (A\text{-}6)$$

and

$$I_2 = e^{-\delta t} \int_0^t x^{\beta} e^{\delta x} dx \qquad (A\text{-}7)$$

which occur as solutions of the mass balance equations, as for example Equation (3-1).

A general form for the solution of these forms may be obtained by the procedure outlined in Section A-1 followed by expansion of the pre-factor exponential in Maclaurin series, subsequent multiplication of the series, collection of terms involving like powers of (δ t) and ultimate simplification.

Thus

$$I_1 = \sum_{m=0}^{\infty} \frac{(\beta t)^m}{m!} \cdot t^{\beta} + 1 \sum_{n=0}^{\infty} (-1)^n \frac{(\beta t)^n}{n!(n+\beta+1)}$$

which, on introduction of the notation for the truncated product

$$\prod_n (\beta + 1 + n) \equiv (\beta + 1)(\beta + 2)(\beta + 3)\ldots(\beta + n + 1)$$

may be reduced to the tractable form

$$I_1 = t^{\beta} + 1 \sum_{n=0}^{\infty} \frac{(\beta t)^n}{\prod_n (\beta + 1 + n)}, \qquad \text{(A-8)}$$

In exactly the same way,

$$I_2 = t^{\beta} + 1 \sum_{n=0}^{\infty} (-1)^n \frac{(\beta t)^n}{\prod_n (\beta + 1 + n)}. \qquad \text{(A-9)}$$

Further, both series (A-8) and (A-9) are seen to be absolutely convergent for all finite β t.

A.3.0 APPLICATION OF EQUATION (A-6) AND (A-7)

To illustrate the utility of the series solutions, several cases are treated. Consider the integral

$$I_a = e^{at} \int_0^t e^{-at} dt$$

which may be directly integrated by elementary methods to yield

$$I = \frac{e^{at} - 1}{a} = \frac{1}{a} \sum_{m=0}^{\infty} \frac{(at)^m}{m!} - \frac{1}{a} = \frac{1}{a} \sum_{m=1}^{\infty} \frac{(at)^m}{m!} = t \sum_{m=0}^{\infty} \frac{(at)^m}{(m+1)!}. \qquad \text{(A-10)}$$

On the other hand, I_a is of the form of Equation (A-6) with $\beta = 0$, hence, from Equation (A-8),

$$I_a = t \sum_{n=0}^{n=\infty} \frac{(at)^n}{\prod_{n} (n+1)}$$

but $\prod_{n} (n+1) = (1)(2)(3)\ldots(n+1) = (n+1)!$

$$I_a = t \sum_{n=0}^{n=\infty} \frac{(at)^n}{(n+1)!} \tag{A-11}$$

which is exactly the form of Equation (A-10).

A second, perhaps more instructive example comes from the evaluation of the integral in Equation (3-1)

$$C(t_f) = 2.08 \times 10^{-13}\, e^{-0.05t} \int_0^{t_f} u^{1.5} e^{0.05u}\, du$$

which is obviously of the form of I_2 (Equation (A-7)) for which the solution is, from Equation (A-9), given as

$$C(t_f) = 2.08 \times 10^{-13}\, t_f^{5.5} \sum_{n=0}^{n=\infty} (-1)^n \frac{(0.05\, t_f)^n}{\prod_{n} (4.5+n)}. \tag{A-10}$$

Consider now, only the sum, which on expansion yields the first several terms as

$$\sum = \frac{1}{4.5} - \frac{(0.05\, t_f)}{(4.5)(5.5)} + \frac{(0.05\, t_f)^2}{(4.5)(5.5)(6.5)} - \frac{(0.05\, t_f)^3}{(4.5)(5.5)(6.5)(7.5)} + \ldots$$

$$= 0.222 - .00202\, t_f + .0000155\, t_f^2 - .0000001036\, t_f^3 \ldots,$$

a result which clearly converges quite rapidly for $t_f \leq 50$ years, which is the time span of interest. Thus, $C(45) = 9.2 \times 10^{-13}$ if one considers only the first three terms in the series. Actually, the result depicted in Table 3.2-1 were carried out utilizing the first five terms of the expansion.

A.4.0 EMPIRICAL EQUATIONS

As is frequently the case, concentrations expressed as functions of time, as for example Equation (A-10), have in the course of additional computations, to be integrated. Examples of this would include Equation (3-10). In this circumstance, the series expansion, such as Equation (A-10) is somewhat cumbersome. To simplify this process, recourse has been had to empirical methods whereby the concentration computed from equations of the form (A-9) are fitted to the equation

$$\ln(C_w) = \alpha + \beta + 1) \ln t - \gamma t$$

which corresponds to the assumption that

$$C_w(t) = \alpha' t^{\beta} + I_{\infty} e^{-\gamma t}$$

The fit is accomplished by a least squares[3] fit to obtain the best value of α' and γ.

The actual form of Equation (3-2) was obtained in the indicated manner.

A.5.0 DERIVATION OF SOLUTION OF EQUATION (5-3)

In general, the form of Equation (5-3) requires a solution given by Equation (5-6) which is of exactly the form of Equation (A-7) which has been shown to have a solution of the form given by Equation (A-9). Unfortunately, the value of $k_2 u$ is so large that the convergence of Equation (A-9) makes the latter quite unsuitable for evaluation. In this case the most useful approach requires a series of transformations as follows:

Equation (5-3) is re-written after substitution of Equation (5-6) for the $C_w(t)$ for Lake Michigan (in terms of the exponential, the factor $k_2 u >> .09t$, so that the latter is ignored), then

$$C_w(t) = \gamma t^{n+1} \tag{5-6}$$

whereupon

$$\frac{C_p(t)}{k_1 \gamma} = e^{-k_2 t} \int_{t=T>0}^{t} e^{k_2 u} u^{n+1} du + \frac{k_4}{k_2 \gamma} e^{-k_2 t} \quad , \tag{5-3}$$

NOW:

$$\frac{C_p(t)}{k_1 \gamma} = e^{-k_2 t} \left\{ \int_0^t e^{k_2 u} u^{n+1} du - \int_0^{T=t>0} e^{k_2 u} u^{n+1} du \right\} + \frac{k_4}{k_2 \gamma} e^{-k_2 t} \quad ,$$

If the following substitutions are made

Let $u = Ts$	$R = T-t$
$\alpha = k_2 T$	$u = RV$
$du = TdX$	$k_2 R = \beta$
	$du = RdV$

then

$$\frac{C_p(t)}{k_1 \gamma} = e^{-\gamma} \int_0^1 e^{\alpha X} T^{n+1} X^{n+1} dX - e^{-k_2 R} e^{-k_2 t} \int_0^1 e^{\beta V} R^{n+1} V^{n+1} dV + \frac{k_4}{k_2 \gamma} e^{-k_2 t} \tag{A-11}$$

$$= \tau^{p+1}\int_0^1 e^{\alpha(X-1)}X^{p+1}dX = e^{-k_1\tau}R^{p+1}\int_0^1 e^{\beta(Y-1)}Y^{p+1}dY + \frac{k_1\lambda}{k_1\gamma}e^{-k_1 t} \qquad (A\text{-}11)$$

A further series of substitutions

$\beta = X = 1-\lambda$	$\alpha = \beta = Y-1$
$X = 1-\lambda$	$Y = 1-\beta$
$dX = -d\beta$	$dY = d\beta$

transforms Equation (A-11) into the form

$$\frac{C_p(t)}{k_1\gamma} = \tau^{p+1}\int_0^1 e^{-\alpha\beta}(1-\beta)^{p+1}d\beta - R^{p+1}e^{-k_1\tau}\int_0^1 e^{-\beta\beta}(1-\beta)^{p+1}d\beta + \frac{k_1\lambda}{k_1\alpha}e^{-k_1 T}, \quad (A\text{-}12)$$

More generally, assume $C_p(t) = \gamma t^p$, then by the same series of transformations, for the case $t > \tau$,

$$\frac{C_p(t)}{k_1\gamma} = \tau^{p+1}\int_0^1 e^{-\alpha(1-X)}X^p dX - R^{p+1}\int_0^1 e^{-\alpha(1-Y)}e^{-k_1\tau Y}Y^p dY \quad , \qquad (A\text{-}13)$$

Note that, for $k_1\tau \gg 0$ and $p > -1$, the second integral is considerably smaller than the first. On the other hand, for very small τ, the contribution from the second integral is of importance.

APPENDIX A REFERENCES

(1) "Modern Analysis," E. T. Whittaker and G. N. Watson, Cambridge, 1948, Chapter 3, pp. 235-264 especially pp. 241ff.

(2) "Advanced Calculus," I. S. Sokolnikoff, McGraw, New York, 1939, pp. 390ff.

(3) "Treatment of Experimental Data," A. G. Worthing and J. Geffner; Wiley, New York, 1943, pp. 56ff.

APPENDIX B

PARTITION COEFFICIENTS FOR AQUEOUS PCB SOLUTIONS

B.1.0 DISTRIBUTION[1,2] *

If a given solute, A, is soluble in two immiscible solvents S and S', then at equilibrium

$$A_{(S)} \rightleftharpoons A_{(S')} \quad ; \tag{B-1}$$

Equation (B-1) expresses the distribution of the available solute A into each of the separate solvents and may be described by the equilibrium constant

$$\rho = \left| \frac{A_{(S')}}{A_{(S)}} \right| \tag{B-2}$$

which is known as the partition or distribution coefficient for the given solute in the two solvents.

B.2.0 MEASUREMENT OF PARTITION COEFFICIENT

Suppose a solute, A, was originally present in solvent S with a concentration C_{1i}. After mixing the original solution with a second solute, S', and allowing the (immiscible) solutions to separate, it is found that the concentration of A in S is C_1, in S' is C_2. If the mass of S is M_1 and that of S' is M_2, then

$$M_1 C_{1i} = M_1 C_1 + M_2 C_2 \quad ; \tag{B-3}$$

By suitable rearrangement and the introduction of ρ from Equation (B-2), Equation (B-3) becomes

$$\rho_{S,S'} = \frac{C_{1i} - C_1}{C_1} \tag{B-4}$$

or alternately

$$\rho_{S,S'} = \frac{M_1}{M_2} C_{1i} - C_2 \quad ; \tag{B-4'}$$

Thus, the partition coefficient for two solutes may be determined either from the concentration change of the solute in the initial solvent due to the "extraction" by the second solvent or by the comparison of the initial concentration to the concentration in the second solvent after the "extraction".

---

* All references for this Appendix are listed on page B-5

B.3.0 TYPICAL PARTITION COEFFICIENTS FOR PCBs

B.3.1 Aqueous/Activated Carbon

Hager and Rizer[3] have studied the effect of granulated activated carbon on PCB solutions (made up in Acetone and diluted with water). Their study included both Aroclor 1242 and Aroclor 1254 PCB preparations. Their data[3] may be summarized as in Table B.3-1:

TABLE B.3-1[3]

PARTITION MEASUREMENTS - PCBs IN WATER/CARBON GRANULES

Carbon Dosage (mg/l)	Aqueous Concentration (ppb) 1242	1254
Control	45	49
2.0	7.3	37
5.0	1.6	17
10.0	1.1	4.2
25.0	ND	1.6
50.0	ND	1.2

Analyses of these data using Equation (B-4') yields the partition coefficients displayed in Table B.3-2:

TABLE B.3-2

PARTITION COEFFICIENTS AQUEOUS PCB/CARBON

Carbon Dosage mg/l	Partition Coefficient p(1242)	p(1254)
2	3.58×10^5	1.1×10^6
5	5.43×10^5	3.3×10^6
10	3.99×10^5	9.7×10^5
25	---	1.1×10^6
50	---	0.73×10^6

B.3.2 Aqueous/Soils and Clays

Haque et al[4] have studied the partition coefficients for aqueous Aroclor 1254 solutions with a number of soil type materials. The results of their work (from their Figure 3[4]) may be summarized as follows in Table B.3-3:

TABLE B.3-3

CALCULATED PARTITION COEFFICIENTS[4] FOR AQUEOUS AROCLOR 1254

SORBENT	$P_{AQ/SORBENT}$
Silica Gel	0.2
Sand (Del Monte)	0.02
Kaolinite Clay	1.0
Montmorillonite Clay (#26)	1.5
Illite Clay (#35)	3.0
Woodburn Soil (Loam)	10

B.3.3 Aquatic Concentration Factors

A number of authors have computed concentration factors for aquatic species. For example, Stalling and Mayer[5], as a result of a number of determinations of accumulation of PCBs, presented the results shown in Table B.3-4:

TABLE B.3-4[5]

ACCUMULATION OF PCBs BY VARIOUS AQUATIC ORGANISMS

Species	Aroclor	Exp. Time	Concentration Factor
Catfish	1248	60 da	7.2×10^4
	1254	60 da	7.6×10^4
Bluegill	1248	60 da	6.37×10^4
	1254	60 da	1.28×10^5
Fiddler Crab	1254	30 da	$2.29 \times 10^5 - 3.4 \times 10^5$
Pink Shrimp	1254	30 da	$6.9 \times 10^5 - 1.2 \times 10^5$

In addition there are reports of fish uptakes equivalent to partition coefficients of 4×10^3 to 9×10^3 in Lake Ontario,[6,7] to 1.9×10^5 in Lake St. Clair,[9] 7×10^3 to 2×10^4 for the Hudson River[9] and 4×10^3 to 5×10^3 in the Atlantic Ocean.[10]

B.3.4 Sediment Concentration Factors

The large number of measurements of sediment concentration factors may be fairly represented by the measurements of Haile, et al[6] on Lake Ontario in 1974 which indicate

$$P_{sed/water} = 1.7 \times 10^3 \text{ to } 2.5 \times 10^4$$

B.3.5 Effect of Organic Content of Sediment on PCB Partition

The experiments with soil leaching characteristics reported by Tucker, et al[11] show the marked effect of organic carbon on the aqueous partition. The manner in which the experiment was conducted and the nature of the explicit results precludes the direct calculation of partition coefficients but the data in their[11] Table II, which is reproduced herein as Table B.3-5, are quite suggestive.

TABLE B.3-5

PCB PERCOLATION STUDIES[11]

HOUSTON LOAM (1% Organic Carbon)		BAY SILTY LOAM (1% Organic Carbon)		DRUMMER LOAM (6% Organic Carbon)	
Elution Vol. (l)	PCB Conc. (ppb)	Elution Vol. (l)	PCB Conc. (ppb)	Elution Vol. (l)	PCB Conc. (ppb)
1.1 - 8.1	ND	2.7 - 16.4	ND	1.6 - 9.9	ND
10.1	ND	20.7	68	13.5	ND
13.6	33	27.6	92	16.6	ND
35.6	63	61.9	153	31.4	ND
48.1	63	98.1	138	59.3	ND

APPENDIX B REFERENCES

(1) "Separation Methods in Chemical Analysis," J.M. Miller, Wiley, New York, 1975, pp. 32ff.

(2) "Quantitative Inorganic Analysis," G. Charlot and D. Bézier; Methuen, London, 1957, pp. 155ff.

(3) Hayes, and Rizzo. EPA Tech. Transfer Session, Atlanta, April 10, 1974.

(4) Hague, R., D.W. Schmedding and V.H. Freed. Environ. Sc. Technol., 8, 439 (1974).

(5) Stalling, D.L. and F.L. Mayer, Jr. Environ. Health Perspectives, 1, 159 (1972).

(6) Haile, C.L., G. Veith, G. F. Lee and W.C. Boyle. EPA-660/3-75-002, June 1975, U.S. EPA.

(7) Kaiser, K.L. Ref, 19, 523 (1974).

(8) Michigan Department of Agriculture, Bureau of Consumer Protection, 1973, Great Lakes Environmental Contaminants Study.

(9) Quoted by D.J. Ruff and V.J. DeCarlo - Private Communication.

(10) Harvey, G.R., H.P. Miklas, V.T. Bowen and W.G. Steinhauer, J. Marine Res., 32, 103 (1973).

(11) Tucker, E.S., W.J. Litschgi and W.H. Neese, "Migration of PCBs in Soil Induced by Percolating Water," Bull. Environ. Contamination & Technol., 13, No. 1, 1975.

APPENDIX C

ENVIRONMENTAL PCB LOAD

C.1.0 INTRODUCTION

In this Appendix a model is presented that proceeds from published[1] data on the production and sales of PCBs within the United States. The sales figures are further subdivided into various use categories. With the introduction of estimated loss factors for each use category, it is possible to construct an equation describing the total environmental PCB load $M_{ev}(t)$. With the further introduction of use life factors for the major use categories, it is then possible to estimate the mobile environmental PCB load, $M_{ev}(t)$. Finally, the introduction probabilities of vaporization, it becomes possible to construct a model of the atmospheric reservoir. The results of the various steps in this computation are compared to the Nisbet and Sarofim[2] estimates.

C.1.1 Empirical Description of Production, Sales and Specific Use Categories

From the data supplied by Monsanto,[1] a portion of which is presented as Table C.1.1-1, it is possible to construct empirical descriptions for the total production, sales and uses in specific use categories.

C.1.1.1 Period 1930-1970

From the Monsanto[1] sales data for PCBs, it is possible to fit an empirical expression for each category which, to a satisfactory degree, represents the time dependence of that parameter. In each case, it is assumed that the relation is of the general form:

$$\ln Q(t) = a + n \ln t, \qquad (C\text{-}1)$$

(a) Total Production

The derived empirical expression for the yearly production takes the form, for the period 1930-1970,

$$Q_{prod}(t) = 2.94 \times 10^{5} t^{1.151} \text{ lbs/yr}, \qquad (C\text{-}2)$$

---

[a]The references for this Appendix are listed on page C-21.

The appropriate empirical expression for the yearly sales, for the period 1930-1970, takes the form

$$Q_{sales}(t) = 311\ t^{3.13}\ \text{lbs/yr}, \qquad \text{(C-3)}$$

The corresponding expressions for capacitor sales and for transformer sales are (for the period 1930-1970)

$$\left.\begin{aligned} &\text{Capacitor sales:} \quad Q_{cap}(t) = 2.03 \times 10^{2}\ t^{3.139}\ \text{lbs/yr} \\ &\text{Transformer sales:} \quad Q_{trans}(t) = 2.03 \times 10^{1}\ t^{3.17}\ \text{lbs/yr} \end{aligned}\right| \qquad \text{(C-4)}$$

In the above expressions, it should be noted that it is explicitly assumed that

(a) the given Monsanto data are accurate and represent the great preponderance of PCB production and sales within the U.S.

(b) the trends noted in the interval 1954-1970 are simple continuations of earlier trends, so that the curves which fit the period 1954-1970 can, in fact, be used to cover the entire interval, 1930-1970.

Information reported elsewhere[3] suggests that the second assumption above might result in low estimates for total U.S. sales; therefore, the results derived from this analysis must be considered as a lower bound on the actual situation.

In any case, numerical evaluation of expressions (C-3) and (C-4) suggest that a weighted average for the proportion of PCB sales that were employed in electrical applications is of the order of

$$\beta = 0.62 \text{ (i.e., 62\%)}. \qquad \text{(C-5)}$$

The remainder of the sales during the period 1930-1970 was for non-electrical applications.

C.1.3 Period 1971-1975

In 1970, Monsanto instituted a voluntary ban[4] on the sales of PCBs restricting their use to electrical applications. As a result of this ban, the empirical relationship appropriate for sales in the post 1970 period is

$$Q'_{sales}(t) = 3.31 \times 10^7 \text{ lbs/yr}. \qquad (C\text{-}6)$$

In addition, during this period essentially 100 percent of PCB production was used for electrical applications; i.e.

$$\beta = 1.00 \ (1970\text{-}1975). \qquad (C\text{-}7)$$

To determine the total sales and total electrical system usage for the period 1930-1975, Equation (C-3) may be combined with Equation (C-6). Integration over the appropriate time frame yields

$$\sum_{1970}^{1975} Q_{sales} = \underline{9.33 \times 10^8} \text{ lbs}$$

and for total electrical system usage, Equations (C-4) and (C-5) with (C-7) may be combined and, on integration, yield,

$$\sum_{1970}^{1975} Q_{electrical}(t) = \underline{7.12 \times 10^8} \text{ lbs}.$$

The balance, 2.21×10^8 lbs, was used in non-electrical applications.

C.2.0 ENVIRONMENTAL LOAD OF PCBs

C.2.1 Introduction

PCBs, or for that matter any other refractory chemical compound, may exist in the environment in two distinct states: (a) that material which is in a form such as to remain localised and thus is not actually available to enter the sensitive portion of the environment, i.e., the biota: and (b) that material which is not so constrained and is thus free to enter the sensitive portion of the environment. This latter portion of the environment load will be referred to as "free" or "wild" PCBs. The significance of the first category lies in the fact that the containment is not of infinite life and thus material in category (a) can and will eventually become a component of category (b). For those compounds for which there exists relatively high rates of degradation within the environment, the category (a) is of somewhat lesser importance than for those refractory compounds for which the only inactivation mechanism is the entrapment with non-available forms, for example, in deep ocean sediments.

In order to estimate the rate of accumulation of PCBs in category (b), it is first necessary to determine the rate of entry of PCBs into the category (a). This will be followed by an analysis that suggests the nature of and the relative importance of the processes by which this total environmental load eventually becomes wild PCBs.

C.2.2 Total Environmental PCB Load, $M_{ev}(t)$

It is assumed that, in any time interval t to $t + \Delta t$, a fraction $\alpha < 1$ of the total sales during that interval was directly lost to the environment due to transport losses, spills and manufacturing losses, for example. It is further assumed that a fraction $\beta < 1$ of the total sales was used in the manufacture of long lived electrical components. If the average lifetime of these electrical components (time of service prior to their being discarded as obsolete) is γ_1 years, then during the time interval t to $t + \Delta t$, an amount

$$\beta\, Q_s(t-\gamma_1)\, \Delta t \qquad \text{(C-8)}$$

will enter the environment as part of category (a). In addition, the direct entry is given as

$$\alpha\, Q_s(t)\, \Delta t, \tag{C-9}$$

The remaining sales $(1-\alpha-\delta)\, Q(t)$ was used in the production of relatively short-lived products, such as carbonless paper, hydraulic fluids, etc., which are assumed to have an average lifetime γ_2 years. Thus, the entry of this material into the total environmental pool is given by

$$(1-\alpha-\delta)\, Q_s(t-\gamma_2)\, \Delta t, \tag{C-10}$$

If the three components of the total environmental load, $M_{BV}(t)$ are summed, the resulting differential equation for $M_{BV}(t)$ becomes, in the limit as $\Delta t \to 0$

$$\frac{dM_{BV}(t)}{dt} = \alpha\, Q_s(t) + (1-\alpha-\delta)\, Q_s(t-\gamma_2) + \delta\, Q_s(t-\gamma_1) \quad . \tag{C-11}$$

To evaluate Equation (C-11) it is important to note that the term $(1-\alpha-\delta)\, Q_s(t-\gamma_2)$ does not contribute to $\frac{dM_{BV}(t)}{dt}$ until a time $t > \gamma_2$ where $t = \alpha = 1930$. Similarly, the term $\delta\, Q_s(t-\gamma_1)$ does not contribute to the change in $M_{BV}(t)$ until a time $t > \gamma_1$ where $t = \alpha = 1930$. Hence, the solution of Equation (C-11) is given as

$$M_{BV}(t) = \alpha \int_{\alpha}^{t} Q_s(t)\,dt + (1-\alpha-\delta) \int_{\gamma_2}^{t} Q_s(t-\gamma_2)\,dt + \delta \int_{\gamma_1}^{t} Q_s(t-\gamma_1)\,dt. \tag{C-12}$$

In order to obtain a numerical evaluation of Equation it is appropriate to note that δ, the fraction of initial sales utilized for electrical applications, is given by Equation (C-8) for the period 1930-1970, and by Equation (C-7) for the post 1970 period.

An estimate of the factor α, the fraction of direct losses, can be obtained by noting that

(a) approximately 10% of the electrical material was lost during transport, production and processing.[5]

(b) approximately 30% of the non-electrical material was lost during transport, production, processing, and use.[6]

Hence,

$$\alpha = (0.1)\ (0.52) + (0.30)\ (.38)$$
$$\alpha = 0.17, \qquad \text{(C-13)}$$

It is further assumed that

$$\bar{\gamma}_1 = 20 \text{ years}^{(7)}$$
$$\bar{\gamma}_2 = 4 \text{ years}^{(8)} \quad , \qquad \text{(C-13')}$$

When the expression for $Q_B(t)$ given by Equation (C-3), coupled with the estimates of α, β, γ, and γ_2, are introduced into Equation (C-11), the total environmental load at some time after 1830, $M_{BV}(t)$, may be computed in three time intervals:

$$\left.\begin{aligned}
&\text{(a) } 0 \leq t \leq \gamma_2,\ M_{BV}(t) = 12.04 t^{1.19} \text{ lbs.} \\
&\text{(b) } \gamma_2 < t \leq \gamma,\ M_{BV}(t) = 70.84 \left\{ 0.17 t^{1.19} + (0.21)(t-4)^{1.19} \right\} \text{ lbs.} \\
&\text{(c) } \gamma_1 < t \quad ,\ M_{BV}(t) = 70.84 \left\{ 0.17 t^{1.19} + (0.21)(t-4)^{1.19} + (0.62)(t-20)^{1.19} \right\} \text{ lbs.}
\end{aligned}\right\} \qquad \text{(C-14)}$$

The numerical results are summarized in Table 2.2-1. It should be noted that, in contradistinction to equations such as Equation (C-3), which represent the yearly sales, Equations (C-14) represent the cumulative load in pounds.

TABLE C.2.3-1

$M_{ev}(t)$ = Environmental PCB Load

Date	t	[From Equation (C-14)] $M_{ev}(t)$ (lbs)	[From Equation (C-14/C-16)] $M_{ev}(t)$ (lbs)
1930	0	0	0
1935	5	1.42×10^5	1.42×10^5
1940	10	3.35×10^5	3.35×10^5
1945	15	2.32×10^6	2.32×10^6
1950	20	9.1×10^6	9.1×10^6
1955	25	2.52×10^7	2.62×10^7
1960	30	6.23×10^7	6.23×10^7
1965	35	1.31×10^8	1.31×10^8
1970*	40	2.54×10^8	2.54×10^8
1975**	45	4.58×10^8	3.76×10^8
1980**	50	7.79×10^8	5.12×10^8

*This value of the total environmental load estimated to be of the order of 2.5×10^8 lbs in 1970 is to be compared to the estimate of 7.8×10^8 lbs by Hiebert and Sarofin[2]. See Section C.2.3.1 for a fuller discussion of this comparison.

**Equation (C-14) is not actually valid for the post 1970 period, but if the voluntary ban had not been imposed, the estimated $M_{ev}(1975)$ would have been as recorded in Table 2.3-1.

C.3.3 Effect of Monsanto's Voluntary Ban on PCB Sales

In the actual situation, as a result of the voluntary Monsanto[4] ban on PCB sales, the expression $M_{BV}(t)$ given by Equation (C-14) must be modified to account for post 1970 sales levels. Thus, for the period 1971 and later,

$$M_{BV}(t > 40) = M_{BV}(t = 40) + \alpha' \int_{40}^{t} Q'(t)dt + (1-\alpha-\delta) \int_{40}^{44} Q(t-4)dt$$

$$+ (1-\alpha'-\delta') \int_{44}^{t} Q'(t-4)dt + \delta \int_{40}^{t} Q(t-20)dt$$

which, on noting that $(1-\alpha'-\delta') = 0$ for the period after 1970 (t=40), and substitution of the forms of $Q(t)$ and $Q'(t)$, becomes on integration,

$$M_{BV}(t > 40) = M_{BV}(t = 40) + (0.1)\left(3.31 \times 10^{8}\right)(t-40) + (0.21)\left(\frac{311}{4.39}\right)\left[(40)^{4.39} - (36)^{4.39}\right]$$

$$+ (0.62)\left(\frac{311}{4.39}\right)\left[(t-20)^{4.39} - (20)^{4.39}\right] \quad , \qquad \text{(C-15)}$$

Equation (C-15) may be simplified to yield ($t \geq 45$),

$$M_{BV}(t \geq 45) = 3.75 \times 10^{9} + (3.3 \times 10^{8})(t-40) + 43.92(t-20)^{4.39} , \qquad \text{(C-16)}$$

C.3.3.1 Comparison of the Results of Equation (C-14) with the Estimates of Nisbet and Sarofim[2]

In 1972, Nisbet and Sarofim[2] provided a rough estimate of the losses of PCBs to the North American environment up to the year 1970 to have been: $3 - 4 \times 10^{8}$ lbs to the atmosphere (largely Aroclor 1254 and 1260 from plastics and 1242 from burning of dumps); $6 - 9 \times 10^{8}$ lbs to fresh and coastal waters (Aroclor 1242-1260); and 4.6×10^{7} lbs into dumps and landfills (largely Aroclor 1242); other losses were assumed to be small. The cumulative losses in the period 1930-1970 were estimated to be

Atmosphere	6×10^7 lbs
Water - fresh and coastal	1.2×10^6 lbs
Dumps and landfills	6×10^4 lbs

making a total environmental accumulation ($M_{ev}(t)$ of an estimated $\underline{7.8 \times 10^6}$ lbs.

On the other hand, returning to Equation (C-3), integration over the period 1930-1970 yields the result

$$Q_s(40) = 311\int_0^{40} t^{1.19}dt = \underline{7.64 \times 10^6} \text{ lbs},$$

clearly then, the Nisbet estimate exceeds the cumulative United States sales up to 1970.

Returning to Equations (C-4) which express the capacitor and transformer sales as functions of time, it is clear that, with an average service life of 20 years, the net amount of PCB still in service in 1970 was

$$(Q_{cap})_{\text{in service (1970)}} = 2.03 \times 10^3\int_{20}^{40} t^{1.139}dt$$

$$= \underline{3.35 \times 10^6} \text{ lbs};$$

while for transformers

$$(Q_{trans})_{\text{in service (1970)}} = 3.02 \times 10^3\int_{20}^{40} t^{1.17}dt$$

$$= \underline{1.36 \times 10^6} \text{ lbs}.$$

Hence, in 1970 of the total U.S. sales[1] of 7.64×10^6 lbs, a sub total of 4.71×10^6 lbs were still in service and thus could not participate in the general environmental pool.

If the material still in service in non-electrical applications in 1970 were ignored, the general environmental pool could not have exceeded

$$7.64 \times 10^8 - 4.71 \times 10^8 = \underline{2.93 \times 10^8} \text{ lbs},$$

a value which compares favorably with that indicated in Table C.2.2.1.

C.3.0 MOBILE OR FREE ENVIRONMENTAL PCBs, $m_{EV}(t)$

C.3.1 General Considerations on Mobile PCBs - $M_{EV}(t)$

To consider the processes by which the general environmental load of PCBs $\left(M_{EV}(t)\right)$ becomes free, i.e., the processes by which $m_{EV}(t)$ is generated, it is necessary to consider that some fraction of the direct losses are in a form such that the lost material immediately becomes mobile; i.e., spills and/or evaporation losses. Further, the non-mobile material is usually encased or enclosed in some sort of container which will eventually be degraded thus allowing the subsequent escape of the component PCB.

The fraction of the total sales that is waste occuring in all production uses of PCBs is $\alpha Q_s(t)$ of which some fraction ϵ is immediately mobile. Thus, in the time interval t to $t + \Delta t$, this component introduces an amount

$$\epsilon\alpha Q_s(t)\Delta t \qquad (C\text{-}17)$$

into the free environmental pool. The remainder $(1-\epsilon)\alpha Q_s(t)$ which enters the environmental reservoir is contained in a state such that the PCB content is gradually released with a time constant $\tau_\ell = 1/\lambda_\ell$. Thus, within the reference interval t to $t + \Delta t$, an amount

$$\lambda_\ell(1-\epsilon)\alpha Q_s(t)\Delta t \qquad (C\text{-}18)$$

enters the mobile pool.

Further, a fraction β of the yearly sales was used to manufacture long lived electrical components, assumed to have a useful life of γ_ℓ years, after which the components are scrapped. Thus, the contribution of this source to the general environmental pool is

$$\beta\, Q_m(t-\gamma_1)\Delta t \qquad \text{(C-19)}$$

The electrical containers in which the PCB is enclosed will eventually decay, with a half life $\tau_1 = 1/\lambda_1$. The additional component entering the mobile reservoir will be, during the reference time interval,

$$\lambda_1 \beta\, Q_m(t-\gamma_1)\Delta t \quad , \qquad \text{(C-20)}$$

Finally, the remainder $(1-\alpha-\beta)Q_m(t)$ was used in the construction of products assumed to have a useful life of γ_2 years, after which they are discarded, thus contributing a component to the general environmental pool:

$$(1-\alpha-\beta)\, Q_m(t-\gamma_2)\Delta t \qquad \text{(C-21)}$$

If as before, it is assumed that these products have a lifetime $\tau_2 = 1/\lambda_2$ against decay, then the contribution to the mobile environmental pool will be

$$\lambda_2 (1-\alpha-\beta)\, Q_m(t-\gamma_2)\Delta t \quad . \qquad \text{(C-22)}$$

On combining Equations (C-17), (C-18), (C-20) and C-22), in the limit $\Delta t \to 0$, the differential equation for $m_{mv}(t)$ becomes

$$\frac{dm_{mv}(t)}{dt} = \varepsilon\alpha Q_m(t) + \lambda_2(1-\varepsilon)\alpha Q_m(t) + \lambda_1\beta Q_m(t-\gamma_1) +$$

$$\lambda_2(1-\alpha-\beta)Q_m(t-\gamma_2) \qquad \text{(C-23)}$$

$$= \left|\varepsilon\alpha + \lambda_2(1-\varepsilon)\alpha\right| Q_m(t) + \lambda_2(1-\alpha-\beta)Q_m(t-\gamma_2) + \lambda_1\beta Q_m(t-\gamma_1)$$

where, from Equation (C-3) $Q_m = 311t^{1.49}$.

On integration of Equation (C-23) and the substitution of the parameters from Table C.3.1-1, with the exception of ε, the result is

TABLE C.3.1-1

Estimated Total Environmental PCB Load ($M_{ev}(t)$)
and Mobile Environmental PCB Load in ($m_{ev}(t)$)

Date	t (years)	$m_{ev}(t)$ [1] (lbs)	$m_{ev}(t)$ corr [2] (lbs)	$M_{ev}(t)$ corr [3] (lbs)
1930	0	0	0	0
1935	5	6.49×10^5		1.42×10^6
1940	10	1.40×10^6		3.35×10^6
1945	15	8.62×10^6		2.32×10^6
1950	20	3.14×10^6		9.1×10^6
1955	25	8.54×10^6		2.62×10^7
1960	30	1.89×10^7		6.23×10^7
1965	35	3.86×10^7		1.31×10^8
1970	40	7.01×10^7	7.01×10^7	2.54×10^8
1975	45	1.19×10^8	8.31×10^7	3.78×10^8
1980	50	1.90×10^8	9.04×10^7	4.66×10^8
1990	60	4.30×10^8	1.07×10^8	8.41×10^8

Notes: (1) From Equation (C-24)
(2) From Equation (C-25)
(3) From Equation (C-15)

$$m_{BV}(t) = 10.84\varepsilon(t)^{5.19} + 1.204(t)^{5.19} + 1.49(t-4)^{5.19}$$

$$+ 0.44(t-20)^{5.19} \qquad \text{(C-24)}$$

where the term t-4 is taken to be zero when $t \leq 4$, and that containing t-20 to be zero when $t \leq 20$.

In order to evaluate $m_{BV}(t)$ it is necessary to determine a useful value for ε as follows: From the definition of ε as that fraction of the initial losses, due to spills, transportation accidents, manufacturing wastes, etc., is immediately free, it would appear that a reasonable choice[9] of ε is 40% of the initial losses. Thus, in terms of this choice of ε, Equation (C-24) becomes

$$m_{BV}(t) = 5.54t^{5.19} + 1.49(t-4)^{5.19} + 0.44\ (t-20)^{5.19}, \qquad \text{(C-25)}$$

The detailed evaluation of Equation (C-25) is enumerated in Table C.3.1-1 which also includes the total environmental load $M_{BV}(t)$ from Equation (C-15) for comparison purposes.

C.3.2 Effect on the 1970 Ban[4] on Mobile PCBs ($M_{BV}(t)$)

It is now appropriate to discuss the effect that the partial ban established in 1970 can be expected to have on the mobile PCB load, $m_{BV}(t)$. The operative change occurs as a result of the substitution of Equation (C-6) for Equation (C-3) in the time interval after 1970. The resulting expression for $m_{BV}(t \geq 40)$ is given as (recalling that the ban also stopped sales for non-electrical applications):

$$m_{BV}(t > 40) = \varepsilon\alpha\beta\int_0^{40} t^{5.19}dt + \varepsilon\alpha(1-\beta)\int_0^{t-40} dt + \lambda_2(1-\varepsilon)\alpha\int_0^{40} t^{5.19}dt$$

$$+ \beta\lambda_1\delta\int_0^{t} (t-\gamma_1)^{5.19}dt + (1-\alpha-\beta)\lambda_2\delta\int_0^{t\leq 44} (t-\gamma_2)dt \qquad \text{(C-26)}$$

which, on integration and evaluation of the coefficients, becomes, using the parametric values listed in Table 2.4.1-1,

$$m_{sv}(t \leq 45) = \left| 7.59 \times 10^7 + (0.44)\ (t-20)^{5.39} + 1.32 \times 10^6\ (t-40) \right| \text{ lbs} \quad \text{(C-26')}$$

Numerical values derived from Equation (C-26') are listed in column 4 of Table 2.4.2-1. Again, the effect of the voluntary partial ban of 1970-71 is apparent.

It will be useful in what follows to express the numerical relationship given by Equation (C-26') in the approximate empirical form (formed by regression analysis of the tabulated values of Equation (C-26')

$$\left.\begin{aligned} m_{sv}(t \leq 40) &= 4.83^{5.5} \\ m_{sv}(t > 40) &= 1.69 \times 10^6 t^{1.95} \end{aligned}\right\} \text{ lbs.} \quad \text{(C-27)}$$

Equation (C-27) suggests that, in 1970, the cumulative mobile PCB reservoir, $m_{sv}(40)$ was of the order of 7.82×10^7 lbs whereas the Nisbet and Sarofim[2] estimate for mobile PCBs (water plus atmospheric load) was of the order of 1.8×10^8 lbs. A plot of Equation (C-27) is presented on Figure C.3-1.

C.4.0 ATMOSPHERIC TRANSPORT

C.4.1 Atmospheric Reservoir of PCBs, $m_a(t)$

Suppose that some fraction θ of the instantaneous addition to the mobile environmental material is vaporized. Then within the interval t to $t + \Delta t$

$$\left[\frac{dm_a(t)}{dt}\right]_0 = \theta \frac{dm_{sv}(t)}{dt} \Delta t\ , \quad \text{(C-28)}$$

Further, suppose that the material contained within the mobile pool is vaporized with a time constant $\tau_1 = 1/\lambda_1$, then the additional component of the atmospheric reservoir is given by

$$\left[\frac{dm_a(t)}{dt}\right]_1 = \lambda_1 m_{sv}(t), \quad \text{(C-29)}$$

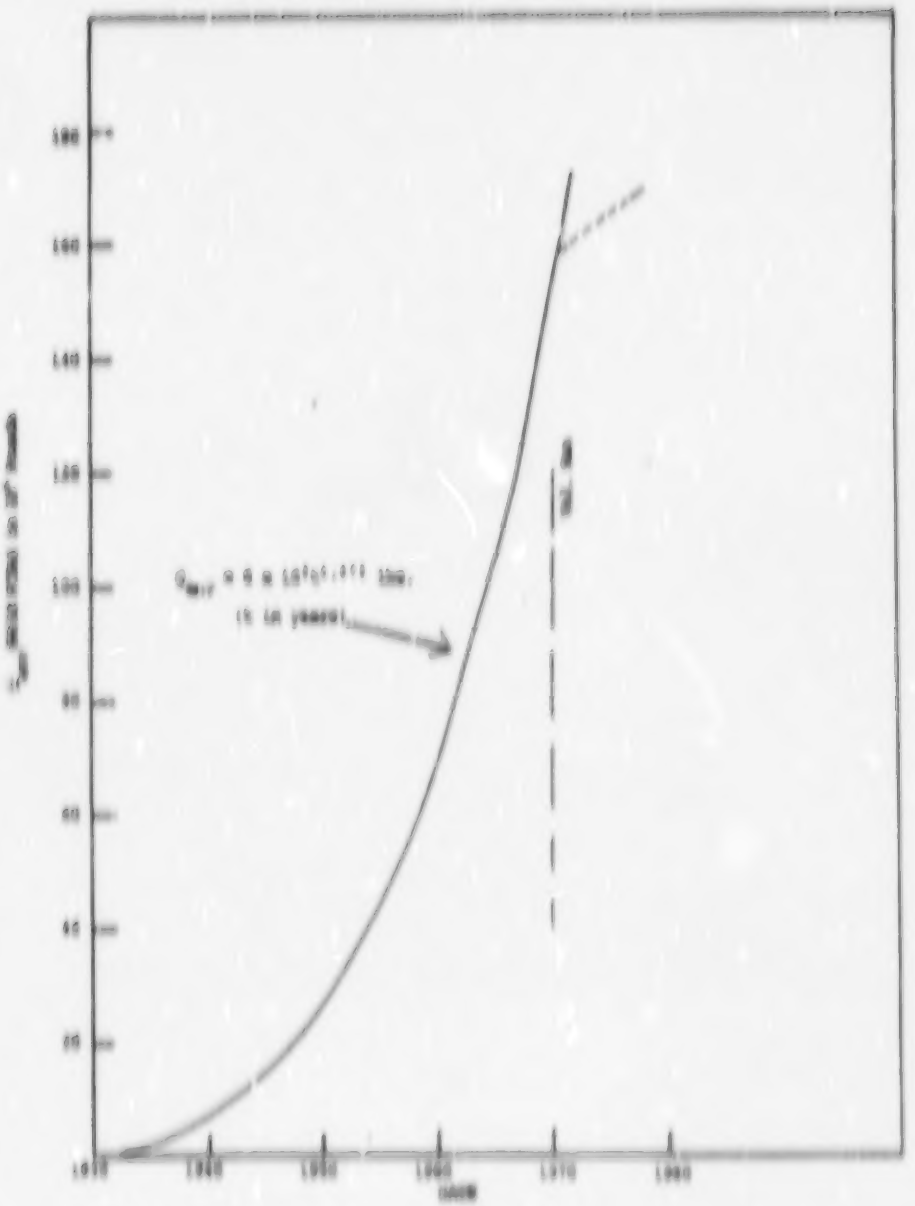


Figure C.3.1
Estimate With PCBs,
$M_{b,y}(t)$ where t = 0, 1930
Equation (C-27)

Table C.4.1-1

Parameter Values for Equation (C-23) and Equation (C-25)

$\alpha = 0.17$	$\varepsilon = 0.40$	$\alpha' = 0.1$
$\beta = 0.62$	$1-\varepsilon = 0.60$	$\delta = 311$
$1-\alpha-\beta = 0.21$		$\delta' = 3.31 \times 10^7$

$\lambda_2 = 0.1$, $T_{1-1/2} = 6.9$ years

$\lambda_1 = 0.01$, $T_{1-1/2} = 69$ years

$\gamma_2 = 4$ years $\gamma_1 = 20$ years

Finally, suppose that the lifetime, $\tau_s = 1/\lambda_s$, of the atmospheric reservoir results in a decay of $m_a(t)$ given as

$$\left[\frac{dm_a(t)}{dt}\right]_c = \lambda_s\, m_a(t). \qquad (C\text{-}30)$$

The total change in $m_a(t)$ with time is then given as

$$\frac{dm_a(t)}{dt} = \left[\frac{dm_a(t)}{dt}\right]_a + \left[\frac{dm_a(t)}{dt}\right]_b + \left[\frac{dm_a(t)}{dt}\right]_c \qquad (C\text{-}31)$$

which on substitution of the appropriate expressions yields the differential equation for $m_{aV}(t)$ as follows:

$$\frac{dm_a(t)}{dt} + \lambda_s\, m_a(t) = 0 \quad \frac{dm_{aV}(t)}{dt} + \lambda_i\, m_{aV}(t) \qquad (C\text{-}32)$$

for which the general solution is

$$m_a(t) = e^{-\lambda_s t}\int_0^t \left[0 \quad \frac{dm_{aV}(t)}{dt} + \lambda_i\, m_{aV}(t)\right] e^{\lambda_s t}\, dt \quad . \qquad (C\text{-}33)$$

After substitution of the expression for $m_{aV}(t)$ from Equation (C-27) the result of the integration by parts is

$$m_a(t) = 4.83\,\frac{\lambda_i}{\lambda_s}\; t^{1/3} + \frac{81}{\lambda_s}\sqrt{74}\left[(0 - \frac{\lambda_i}{\lambda_s}\right]t^{1/3}\left\{1 - \frac{1/3}{\lambda_s t} + \frac{(1/3)(2/3)}{(\lambda_s t)^2}\right.$$

$$\left. - \frac{(1/3)(2/3)(1/3)}{(\lambda_s t)^3}\, e^{-\lambda_s t}\int_0^t t^{-1/3} e^{\lambda_s t}\, dt\right\} \qquad (C\text{-}34)$$

In order to evaluate Equation (C-34), it is appropriate to return to the source term for $m_a(t)$, via, Equation (C-28) and (C-29), then

$$\sum_{44}^{44} m_a(t) = \int_0^t \left[\theta \frac{dm_{BV}(t)}{dt} + \lambda_1 m_{BV}(t) \; dt \right] \qquad (C-35)$$

which, upon substitution of the form of $m_{BV}(t)$ from Equation (C-27), yields the expression

$$\sum_{44}^{44} m_a(t) = 7.82 \times 10^7 \left\{ \theta + 7.27\lambda_1 \right\} \text{ lbs} \qquad (C-36)$$

If now, the Nisbet and Sarofim[2] estimate of total atmospheric load of 6×10^7 lbs is introduced, using the same factor of 3 to account for the overestimate, and assuming that $\theta = .05$, Equation (C-36) may be solved for λ_1 to yield

$$\lambda_1 = 0.0283 \text{ yr}^{-1}$$

$$\text{or } \underline{t_{\frac{1}{2}} = 35.3} \text{ years.}$$

Thus, it appears that the modified Nisbet and Sarofim[2] estimate of the cumulative atmospheric load requires that the time for the evaporation losses of the environmental load to reduce the latter to 1/e is of the order of 35.3 years.

C.4.2 Atmospheric Concentration of P-Bs

If Equation (C-35) is evaluated for $t = 45$ and also for $t = 44$, then

$$\sum_{44}^{44} m_a(t) - \sum_{44}^{44} m_a(t) = \overline{m_a}(1975) = 2.51 \times 10^6 \text{ lbs}.$$

Whereupon, returning to Equation (C-34) and evaluating at $t = 45$ with the appropriate substitution for θ and for λ_1, yields the expression for λ_2

$$\lambda_2^2 - 1.23\lambda_2^{\frac{1}{2}} + 0.15\lambda_2 - 0.117 = 0 \qquad (C-37)$$

which is in the form

$$\lambda^3 + b\lambda^2 + c\lambda + d = 0$$

for which[10]

$$\Delta = 18\,bcd - 4b^3d + b^2c^2 - 4c^3 - 27d^2 = -0.3696 < 0$$

hence, only one of the roots of Equation (C-37) is real, and that real root is

$$\lambda_1 = 1.1865\ yr^{-1}$$

$$\frac{1}{\lambda_1} = \tau_1 = 0.843\ yrs. \qquad (C\text{-}38)$$

Returning to Equation (C-34), substituting for θ, λ_1 and λ_1, and evaluating the integral by the methods of Appendix A, yields

$$m_s(45) = 2.05 \times 10^5\ lbs. \qquad (C\text{-}39)$$

If it is now assumed that the air concentration over the continental United States is uniform, and that the atmosphere is of uniform density and hence of height[11]

$$h_{is} = 8.18 \times 10^3\ meters.$$

The area of the continental United States[12] $= 1.827 \times 10^{13} m^2$; whereupon the concentration of PCB in 1975 should have been

$$\overline{C_{air}}(45) = \frac{2.05 \times 10^5 \times 454}{8.18 \times 10^3 \times 7.82 \times 10^{13}}$$

$$\overline{C_{air}}(1975) = 1.45 \times 10^{-9}\ gm/m^3 = 14\ ng/m^3$$

or in the usual concentration terms, gm/gm,

$$\overline{C_{air}}(1975) = 11\ ppt.$$

Actual measurements by Murphy[13] in 1975-1976 have shown that ambient PCB levels were of the order of 3-6 ppt indicating that the estimate in Equation (C-37) is within a factor of two to three of the measured values. This reasonable agreement supports the validity of the estimates for the various particulates used in this analysis.

C.5.0 TIME DEPENDENCE OF $\sigma(t)$ and $B(t)$

Returning to Equation (C-34) and introducing the definition of $\sigma(t)$ as

$$\sigma(t)A = \lambda_s m_s(t) \tag{C-38}$$

where A = area of continental United States.

By iterated calculation of Equation (C-38) for various times from t = 0 (1930) to t = 40 (1970) and by standard regression analysis of the result, the empirical form for $\sigma(t)$ is

$$\sigma(t) = \sigma_0 t^{1.6} \tag{C-39}$$

and since, at least for the Great Lakes, fallout constitutes the major PCB input, the forcing function, B(t) is taken to have the form

$$B(t) = a'' t^{0.5}, \tag{C-40}$$

APPENDIX C REFERENCES

(1) Monsanto Industrial Chemicals Company, "PCB Manufacture and Sales-Monsanto Industrial Chemicals Company - 1957 thru 1964." (unpublished data), 1974a.

Monsanto Industrial Chemicals Company, "PCB Manufacture and Sales-Monsanto Industrial Chemicals Company - 1965 thru 1974." (unpublished data), 1974a.

(2) Nisbet, C.T., and A.F. Sarofim. Environmental Health Perspectives Exp 1: 21-38, 1972.

(3) Versar Inc., "PCBs in the United States: Industrial Use and Environmental Distribution" NTIS PB-252 402/3WP. February 1976.

(4) Monsanto Industrial Co., Testimony, FMRX(307) Docket No. 1, Presented by Mr. W.B. Papageorge.

(5) Ibid, Reference 3, Section V, 3.1 and 3.2.

(6) Ibid, Reference 3, Section V, 3.5.

(7) Ibid, Reference 3, Section V, 3.1 and 3.2.

(8) Ibid, Reference 3, Section V, 3.5.

(9) Ibid, Reference 3, Section II, 5.0.

(10) I.S. and E.S. Sokonnikoff, "Higher Mathematics for Engineers and Physicists," McGraw, 1941, New York.

(11) Iso Density Atmosphere.

(12) Anon., World Almanac, Washington Star News, Washington, D.C., 1975.

(13) Murphy, Thomas. Private communication.

APPENDIX D

CUMULATIVE ENVIRONMENTAL PCB LOAD AND AN
ESTIMATE OF THE CHLORINE SPECTRUM OF FUTURE PCBs

D.1.0 INTRODUCTION

It has been assumed, in the development of the mass balance model, that there are no significant degradation processes, either environmental nor biological, operative for free PCBs. It will be shown in what follows that the often cited[1,2,3]* observation that, in spite of the fact that Aroclor 1242 was used in many applications which should tend to allow its escape into the environment, the observed PCB spectrum from many biological and environmental specimens most closely resembles that of 1254, it is not necessary to involve degradation or metabolic processes to account for this observation. In point of fact, it is possible to construct a model of the free PCB chlorine content simply from the Monsanto data on sales and end use coupled with estimates of yearly loss factors for each end use category.

D.2.0 PCB SALES BY END USE CATEGORY, Period (1930-1975)

The production and sales figures for the principle Aroclors for the period 1957 through 1975 indicate that, by far the principle species manufactured and sold were the Aroclors 1242, 1248, 1254 and 1260. These mixtures will be the only ones considered in what follows.

It will be necessary to estimate the PCB production and sales in the period 1930 through 1956, a time span for which there appear to exist no official figures.[4] This extrapolation is accomplished by fitting the published production and sales figures, by Aroclor category, for the period 1957 through 1970 by an expression of the form

$$Q(t) = at^n \text{ (lbs/yr)} \qquad \text{(D.1)}$$

and then assuring that this expression fits the corresponding production and sales figures back to 1930 when t = 0 in 1930 (t in years). The Monsanto released sales figures[4] also allow the estimate of the proportional use factors for each end use for each of the Aroclors. The results of these calculations are displayed in Table D.2-1 which follows.

From the computed use factors in Table D.2-1, and the sales by end use category it is possible to estimate the quantities of each of the significant

---

*The references for this Appendix are listed on page D-15.

TABLE D.2-1

PROPORTIONAL USE FACTORS - PCBs
(Monsanto Data)[4]

Date	Heat Transfer & Hydraulic Fluids	MSC Industrial	Transformers & Capacitors	Plasticizer Applications
1930-1956	0.025	0.156	0.806	0.013
1957	0.049	0.022	0.784	0.145
1958	0.059	0.039	0.760	0.15
1959	0.086	0.050	0.718	0.146
1960	0.072	0.044	0.707	0.177
1961	0.109	0 056	0.592	0.242
1962	0.107	0.044	0.614	0.235
1963	0.118	0.040	0.600	0.241
1964	0.121	0.038	0.614	0.230
1965	0.113	0.036	0.626	0.226
1966	0.102	0.030	0.640	0.228
1967	0.100	0.023	0.653	0.214
1968	0.128	0.020	0.632	0.221
1969	0.165	0.016	0.552	0.245
1970	0.154	0.022	0.555	0.267
1971	0.136	0.015	0.766	0.082
1972	0.028	---	0.972	---
1973	---	---	1.00	---
1974	---	---	1.00	---

Arrolors utilized in end use. The results of these estimates are shown in Tables D.2-2 through D.2-5. It is to be noted that after the voluntary ban[5] on PCB sales for non-closed end uses in 1970-1971, the form of the empirical description of the various sales categories is

$$Q(t) = \beta \qquad \text{lbs/yr} \qquad \text{(D-2)}$$

and was essentially constant.

Table D.2-1

USE CATEGORIES ARROLOR 1242[4]

(Thousands of Pounds)
(Proportional Images from Table D.2-1)

Date	Heat Transfer (lbs)	Hydraulic Fluids (lbs)	Misc. Industrial (lbs)	Transformers (lbs)	Capacitors (lbs)	Transformers & Capacitors (lbs)	Plasticizers (lbs)	Petroleum Applications (lbs)
1930-1956	---	2,050	13,790	---	---	60,075	10,697	---
1957	---	893	401	7,089	9,963	16,891	1,900	---
1958	---	816	303	6,397	9,650	7,937	1,567	---
1959	---	1,169	680	6,997	7,166	9,763	1,985	---
1960	---	1,310	901	6,094	6,770	12,865	1,221	---
1961	---	2,161	1,110	5,311	6,426	11,738	4,798	---
1962	82.6	2,127	2,127	4,337	8,344	12,681	4,854	---
1963	278	1,907	740	3,535	7,571	11,106	4,461	---
1964	493	1,857	898	4,198	10,877	14,473	5,431	---
1965	757	2,808	1,133	5,266	14,474	19,740	7,196	---
1966	1,187	3,048	1,187	5,973	19,343	25,316	9,019	---
1967	1,560	3,176	990	7,021	20,494	28,115	9,214	---
1968	1,149	2,992	897	7,984	20,363	28,347	9,913	---
1969	2,041	6,448	736	8,172	17,025	25,064	11,183	951
1970	2,834	4,907	1,069	8,143	17,783	25,926	12,973	---
1971	1,933	934	315	6,438	9,660	16,085	1,782	---
1972	20.4	---	---	---	---	708	---	---
1973	---	---	---	---	---	6,200	---	---
1974	---	---	---	---	---	6,207	---	---

TABLE D.2-1

USE CATEGORIES ANNEXOR 1248

(In Thousands of Pounds)
[Proportional Uses Calculated from Table D.2-1]

Date	HYDRAULIC & HEAT TRANSFER		PLASTICIZER APPLICATIONS		MISC. INDUSTRIAL	
	Fract.	Amt. (lbs)	Fract.	Amt. (lbs)	Fract.	Amt. (lbs)
1930-1957	.128	2,043	.804	12,830	.067	1,069
1957	.227	404	.671	1,194	.102	181
1958	.248	635	.63	1,612	.122	312
1959	.305	1,032	.515	1,753	.177	599
1960	.246	695	.605	1,710	.150	424
1961	.268	1,078	.595	2,394	.138	555
1962	270	935	.615	2,130	.115	398
1963	.268	1,343	.628	3,148	.104	521
1964	.272	1,425	.625	3,274	.103	540
1965	.254	1,414	.644	3,584	.103	573
1966	.218	1,093	.691	3,465	.091	456
1967	.238	1,120	.688	3,236	.074	348
1968	.270	1,321	.670	3,279	.061	299
1969	.315	1,790	.643	3,635	.042	237
1970	.259	1,055	.685	2,790	.056	228
1971	.312	81	.582	152	.106	28
1972		---		---		---
1973		---		---		---
1974		---		---		---

TABLE D.2-5

USP CATEGORIES AROCLOR 1260

(Thousands of Pounds)
(Proportional Factors Derived From Table D.2-1)

Date	Hydraulic Fluids (lbs)	Plasticizers (lbs)	Transformers (lbs)	Misc. Industrial (lbs)
1930-1956	423	230	13,529	2,638
1957	493	400	6,085	250
1958	293	897	4,546	173
1959	569	966	4,752	331
1960	520	1,297	5,182	323
1961	713	1,583	3,872	366
1962	679	1,550	4,049	290
1963	900	1,838	4,576	305
1964	1,033	1,963	5,240	324
1965	659	1,318	3,690	6.2
1966	599	1,340	3,760	176
1967	706	1,373	4,190	150
1968	672	1,161	3,319	109
1969	732	1,088	2,450	181
1970	807	1,306	2,714	108
1971	235	141	1,321	26
1972	8.5	---	296	---
1973	---	---	---	---
1974	---	---	---	---

D.3.0 PCB LOSSES TO THE ENVIRONMENT

Now in order to estimate the amounts of the various Aroclors that have escaped to the environment, it is appropriate to introduce a reasonable estimate of the yearly losses associated with each end use. The loss factors, listed in Table D.3-1 include spillage losses accompanying manufacture or use of the PCB containing end product as well as losses due to inadequate disposal methods.

TABLE D.3-1

ESTIMATED LOSS FACTORS FOR PCBs BY END USE[6]

Use Category	% of Yearly PCB Use Lost to Environment
Closed electrical systems (transformers and capacitors)	5%
Hydraulic and heat exchange fluids	60%
Plasticizers	25%
Miscellaneous industrial applications	90%

Each of the assigned loss percentage factors can be the subject of considerable controversy. Suffice it to say that the choices made appear to be reasonable based on the widely varying information considered.

Now, the quantities of PCB of the separate Aroclor mixtures given in Tables D.2-2 through D.2-5, may be combined with the loss factors from Table D.3-1 to yield an estimate of the yearly PCB losses to the environment as well as an estimate of the cumulative total losses. The results of these calculations are listed in Table D.3-2.

The tabulated results in Table D.3-2 may be fitted by the empirical relationship (1930-1970)

$$(Q_{ev})_{cumulative} = 8.0 \times 10^3 \, e^{0.07t} \text{ lbs} \qquad (D\text{-}3)$$

TABLE D.3-2

PCB ENVIRONMENTAL LOAD BY AROCLOR TYPE
(In Thousands of Pounds)

	Aroclor Type					
	1242	1248	1254	1260	1016	Total PCBs
1930-56	18,700	5,395	5,003	3,559	-	32,466
1957	1,991	704	676	932	-	4,303
1958	1,431	1,065	917	783	-	4,196
1959	2,298	1,397	1,142	1,118	-	6,155
1960	2,955	1,126	989	1,191	-	6,361
1961	4,082	1,745	1,295	1,347	-	8,469
1962	3,998	1,452	1,222	1,258	-	7,924
1963	3,648	2,062	1,166	1,503	-	8,379
1964	4,597	2,160	1,224	1,664	-	9,645
1965	5,928	2,260	1,456	1,096	-	10,740
1966	7,010	1,932	1,247	1,041	-	11,230
1967	7,442	1,794	1,158	1,111	-	11,505
1968	7,789	1,881	1,615	954	-	12,239
1969	9,182	2,190	2,172	997	-	14,541
1970	10,072	1,536	2,575	1,044	-	15,227
1971	3,232	112	717	266	167	4,494
1972	48	-	229	20	1,045	1,342
1973	310	-	399	-	1,177	1,886
1974	310	-	309	-	1,098	1,717
				Grand Total =		172.8 x 10^3 lbs.

D.4.0 ESTIMATED CHLORINE DISTRIBUTION OF FREE PCBs

The approximate molecular composition of the Aroclors displayed in Table D.4-1. From the compositional data in Table D.4-1 and the estimated losses by Aroclor type from Table D.3-2 it is possible to estimate the losses as a function of chlorine number. The results of these estimates are displayed in Table D.4-2.

Finally, the estimates contained in Table D.4-2 may be converted to estimates of the average molecular makeup of the environmental PCB load. The results of such computations for selected years between 1930 and 1974 are displayed in Table D.4-3.

D.5.0 RESULTS

By comparison of the estimated molecular composition of the environmental PCBs given in Table D.4-3 with the measured composition given in Table D.4-1 it is evident that the wild PCBs approximate the composition of Aroclor 1248.

The comparison of the estimated chlorine content of the known Aroclors is shown in Table D.4-4.

TABLE D.4-1

APPROXIMATE MOLECULAR COMPOSITION
OF SELECTED AROCLORS[7]

Chlorobiphenyl	Aroclor Type or Grade					
	1221	1242	1248	1254	1260	1016
	(percent composition)					
$C_{12}H_{10}$	11	<0.1		<0.1		<0.1
$C_{12}H_9Cl$	51	1		<0.1		1
$C_{12}H_8Cl_2$	33	16	2	0.9		20
$C_{12}H_7Cl_3$	4	49	18	1		57
$C_{12}H_6Cl_4$	1	25	40	21		21
$C_{12}H_5Cl_5$	0.5	8	36	48	12	1
$C_{12}H_4Cl_6$	ND	1	4	23	38	<0.1
$C_{12}H_3Cl_7$	ND	<0.1		6	41	ND
$C_{12}H_2Cl_8$	ND	ND		ND	8	ND
$C_{12}H_1Cl_9$	ND	ND		ND	1	ND
$C_{12}Cl_{10}$	ND	ND		ND		ND

TABLE D.4-2

CUMULATIVE INCREMENTAL PCB LOAD
BY CHLORINE CONTENT

(In Thousands of Pounds)

	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total
1956	561	2540	6210	8221	8936	4017	1759	285	36	32,565
1957	621	2813	6894	9174	10010	4709	2182	360	45	36,868
1958	664	3020	7487	10130	11311	5419	2558	423	53	41,064
1959	733	3351	8417	11584	13086	6399	3085	512	64	47,219
1960	822	3760	9465	13070	14805	7344	3632	607	89	53,580
1961	944	4326	10922	15135	17128	8529	4162	715	89	62,049
1962	1064	4874	12301	17048	19279	9640	4751	816	102	69,973
1963	1173	5389	13693	19095	21575	10835	5437	936	117	78,352
1964	1311	6030	15369	21473	24160	12153	6192	1069	134	87,997
1965	1469	6846	17436	24315	27123	13391	6728	1157	145	98,735
1966	1609	7796	19747	27328	30097	14568	7230	1240	155	109,966
1967	1922	8799	22154	30406	33080	15754	7755	1329	166	121,471
1968	2156	9850	24674	33673	36376	17053	8243	1405	176	133,710
1969	2431	11008	27639	37543	40368	18635	8782	1495	186	148,251
1970	2733	12428	30735	41462	44523	20362	9365	1569	196	163,478
1971	2837	12880	31723	42624	45657	20840	9517	1590	199	167,972
1972	2881	13073	32131	43086	45782	20928	9539	1592	199	169,314
1973	2938	13324	32643	43700	46046	21076	9563	1592	199	171,204
1974	2992	13561	33163	44272	46265	21193	9582	1592	199	172,821

TABLE D.4-1

[illegible] SPECTRUM OF CHLORINE
[illegible] FOR WILD PCBs

(In Percent)

	Weight Percentage of Isomers Containing Cl_x								
	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9
1956	1.7	7.8	19.1	25.2	27.4	12.3	5.4	0.9	0.1
1960	1.5	7.0	17.7	24.4	27.6	13.7	6.8	1.1	0.1
1965	1.5	6.9	17.7	24.6	27.5	13.6	6.8	1.2	0.1
1970	1.7	7.6	18.8	25.4	27.2	12.5	5.7	1.0	0.1
1974	1.7	7.2	19.2	25.6	26.8	12.3	5.5	0.9	0.1
Average Values	1.6	7.4	18.5	25.0	27.3	12.9	6.0	1.0	0.1

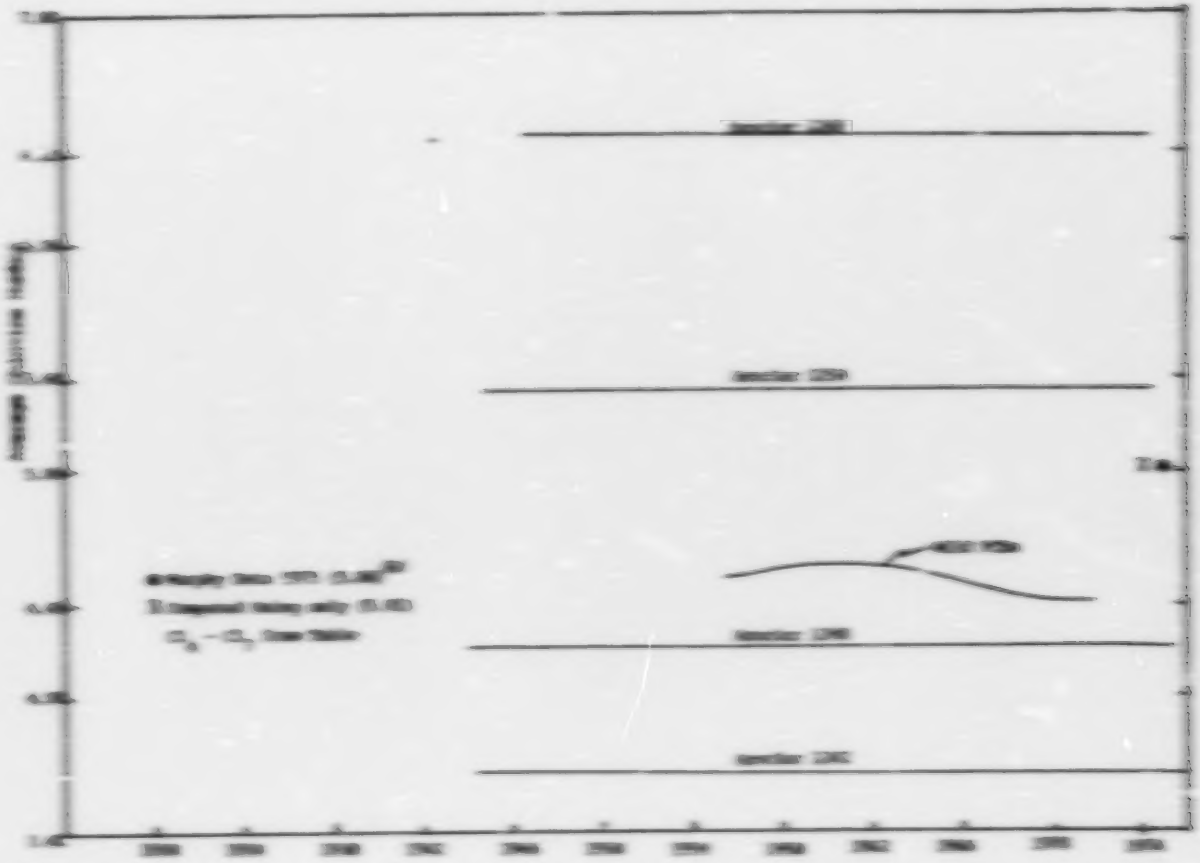


Figure 3.4-1

TABLE D.4-4

CHLORINE CONTENT OF AROCLORS
AND OF ENVIRONMENTAL PCBs

Aroclor	Chlorine Content (atoms/biphenyl)
1242	3.67
1248	4.23
1254	5.35
Environmental	4.32

Thus, from this simple computation it is clear that the spectrum of the environmental PCBs may have arisen simply from the mechanics of the dispersal of the individual Aroclor mixtures and does not necessarily require the invoking of metabolic or environmental degradation processes.

APPENDIX D - REFERENCES

(1) Nisbet, C.T., and A.F. Sarofim. Environmental Health Perspectives Exp I: 21-38, 1972.

(2) Peakall, D.B., "PCBs and their Environmental Effects", CRC Review 5, Issue 4, 1975.

(3) Glooschenko, W.A., et al, "Distribution of Pesticides and PCBs in Water, Sediments and Seston of the Upper Great Lakes", Pest. Monit. J., 10, 61(1976).

(4) Monsanto Industrial Chemicals Company, "PCB Manufacture and Sales-Monsanto Industrial Chemicals Company - 1957 thru 1964," (unpublished data), 1974a.

Monsanto Industrial Chemicals Company, "PCB Manufacture and Sales-Monsanto Industrial Chemicals Company - 1965 thru 1974," (unpublished data), 1974a.

(5) Ibid, Ref. D-1

(6) Versar Inc., "PCBs in the United States: Industrial Use and Environmental Distribution" NTIS PB-252 402/BAP, February 1976.

(7) Hutzinger, O., S. Safe, and V. Zitko, "The Chemistry of PCBs", CRC Press, Cleveland, Ohio, 1974.

(8) Murphy, Thomas, DePaul U., personal communication.

APPENDIX B
DATA BASE FOR LAKE MICHIGAN MODEL

APPENDIX B

BACKGROUND DATA USED TO CONSTRUCT
THE MODEL FOR PCBs IN LAKE MICHIGAN

Table B-1

Concentration of PCBs in Sediments
Along the Southeastern Shore of Lake Michigan (1970-1971) (1)**

Sample Locations	PCBs (ppb)	
Along SW shore of lake; sampling	13.09 A	15.24 B
1-3 mi. off-shore* (See Figure B-1).	6.73 A	16.09 ?
	11.81 ?	12.69 ?
	16.07 A	23.53 A
	87.98 A	17.53 A
	130.27 ?	36.7 ?
	26.61 B	98.81 A
	64.32 A	41.06 A
	3.72 A	132.61 A
	1.87 A	80.63 ?
	35.8 A	29.29 A
	8.31 A	13.34 A
	Total = 896.01	
	Ave. (PCB) = 37.3	

NOTE: Estimated location of sampling sites with respect to thermocline:

A = Above thermocline
B = Below thermocline
? = Questionable

*Sampling sites are located in an area with several known STP discharges. Data were not available on PCB concentrations in these STP effluents; however, judging from PCB data for other area STPs, it is probable that these plants discharge PCBs, thereby producing higher concentrations in the adjacent sediments.

**The references for this Appendix are listed on Page B-17.

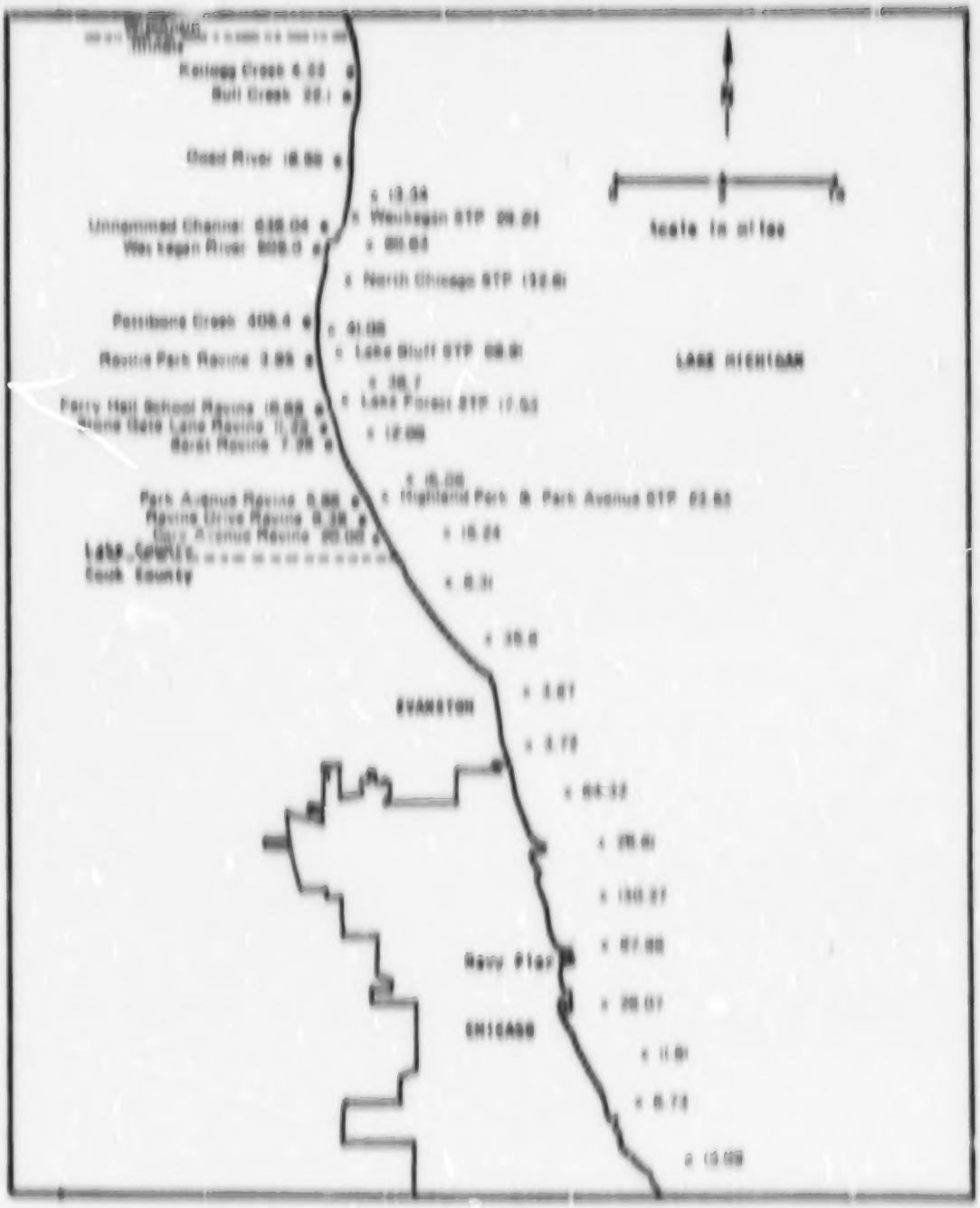


FIGURE E-1

PCBs in sediments of Lake Michigan and in Tributary stream and ravine sediments in 1971. Total of Aroclors 1242 and 1254 in parts per billion on a dry weight basis. (1)

TABLE - B-2

Concentration of PCBs in Reported
Illinois NPDES Effluents Discharging to Lake Michigan[1]

NPDES Location	Flow (mgd)*	PCBs (ppb)**	PCB Load (lb/day)
Waukegan	0.002	2.635	.00004
North Chicago Plant	1.2	0.931	.0083
Total	1.202		0.00834

PCB Load = 0.14×10^{-3} lb/day = 1.04 lb/yr.

---

* Data for 1975

** Data for 1971

NOTE: A major potential source of PCBs released to Lake Michigan has been identified in Waukegan, Illinois.[a] An industrial plant located approximately one mile from Lake Michigan used PCBs in die casting machines for about 20 years, closing in 1972 when PCBs were no longer available in Monsanto. Direct discharges from this plant occurred into the Waukegan Harbor and into a unnamed ditch

---

(a) Great Lakes Surveillance Branch, PCB's in the Bottom Sediments of Waukegan Harbor, Waukegan, Illinois - sampled: May 12, 1976 and June 9, 1976, U.S.E.P.A. Region V.

discharging directly into Lake Michigan. Quantitative estimates of the fate of the PCBs used in this plant are speculative, but more than 100,000 lbs. of PCBs may have been discharged by this plant into drainage ditches and sewers[a]. High levels of PCBs have been found in the sediments of the harbor, the ditch, and of the Waukegan River which drains into Lake Michigan just south of the harbor.

Recent measurements of PCB concentrations in the sediment of Waukegan Harbor vary from 4200 mg/kg at the upper end of the harbor near the industrial discharge point to 11 mg/kg at the lower end of the harbor.[a] Concentrations of PCBs in the connecting channel sediments are 1 to 3 mg/kg, and the concentration of PCBs in the sediment off the end of the piers was measured at 0.1 mg/kg. There is little water flow through this harbor, the drainage area being no more than a few times the water area of the harbor. The high gradient in concentrations of PCBs from the upper to the lower end of the harbor is consistent with the hypothesis that PCBs are strongly bound to the sediments and that the sediments, when undisturbed, provide a reliable sink for the PCBs. (Note: rapid exchange of PCBs between the sediment and overlying water would be expected to be reversible. This would result in a fairly even concentration of PCBs throughout the harbor due to diffusion, since water flows through the harbor but suspended solids settle rapidly at the upper end of the harbor).

Although it is not directly connected to the drainage area of the industrial plant that released PCBs to the Waukegan Harbor, the Waukegan River also has been noted as having appreciable levels of PCBs in the sediments and water. It has been estimated[b] that the concentration of PCBs in Waukegan River water

---

(a) Great Lakes Surveillance Branch, PCB's in the Bottom Sediments of Waukegan Harbor, Waukegan, Illinois - sampled: May 12, 1976 and June 9, 1976. U.S.E.P.A. Region V.

(b) Robert A. Schacht, Pesticides in the Illinois Waters of Lake Michigan, EPA Report 660/3-74-002, Jan., 1974. See particularly Table 7 of this report.

showed a maximum of about 2.6ppb (total of 1242 and 1254) in 1971. If the vital parameters of the river are taken to be [c]

Drainage area 9.68 mi^2

Annual rainfall runoff 10^9/yr.

Then the total outfall of water per year from the Waukegan River into the lake was:

$$Q(lb/yr) = 9.68\ (mi^2) \times (5.28\times10^3)^2(ft^2/mi^2) \times \frac{10^9\ (ft^3/yr)}{12\ (ft/ft)}$$
$$\times 62.4\ lb/ft^3$$
$$= 1.7 \times 10^{13}\ (lbs/yr)$$

Therefore, in terms of the reported maximum PCB concentration [b], the total input of PCBs to Lake Michigan during 1971 from the Waukegan River was on the order of 36.5 lbs. Clearly, this contribution is not trivial, but on the other hand is small compared to the other input of PCBs that are discussed above.

The fact that so small a portion of the PCBs that are available within the sediments are actually found in the overlying waters seems to bear out the often repeated conclusion of this paper that such materials that are contained within the sediments are probably "removed" from further participation in biological processes.

The third possible source of PCBs to Lake Michigan in the Waukegan area is a drainage ditch which runs from the PCB using plant directly with Lake Michigan north of Waukegan harbor. This ditch is about ten feet wide and three feet deep and carries storm sewer runoff from part of the city of Waukegan. In addition, this ditch received the floor drainage from one half of the PCB using plant during the years that PCBs were used. The sediments in this ditch have been found to contain PCBs at a concentration greater than that in the sediments

---

(b) Robert A. Schacht, Pesticides in the Illinois Waters of Lake Michigan, EPA report 660/3-74-002, Jan., 1974. See particularly Table 7 of this report.

(c) Private communication from Mr. Lathrop, U.S. Geological Survey, Reston, Va.

in Waukegan Harbor. However, because of the scouring action of occasional heavy flows in this ditch, much contaminated sediment may have been carried into Lake Michigan. Measurements of PCB levels in the lake sediments show elevated concentrations of PCBs around and particularly south of Waukegan (See Figure E-1). This would be the pattern expected if occasional flows of heavy PCB contaminated sediments were carried into the lake by storm water runoff. The fact that the PCB contamination of the lake sediments is found to be still fairly localized six years after PCBs use has stopped, suggests that the PCBs are fairly immobilized in the sediments. However, since no good estimates of PCB in flow to the lake from the drainage ditch are available, the figures we have used as the basis for total PCB inputs to Lake Michigan must be judged on the basis of reasonableness, and must be considered as subject to possible major revision as more data becomes available.

Table B-1

Concentration of PCBs in Michigan Streams Tributary to Lake Michigan[2,3,4]

Stream	PCB (wtd. mean 1971-72)	Stream Discharge (1974) (CFS)	(1974) (MGD)	PCBs lb/day	PCBs lb/yr
St. Joseph	0.013	4,204	2,716	0.29	105.9
Kalamazoo	0.065	2,162	1,397	0.75	270.1
Grand	0.041	5,814	3,756	1.28	466.5
Muskegon	0.010	2,499	1,608	0.13	47.5
Manistee	0.014	2,047	1,322	0.15	54.8
Boardman	0.017	187	121	0.02	7.3
Elk	0.012	575	371	0.04	14.6
Portage	0.47*	18	12	0.045	16.5
TOTAL		17,478	11,291		986.2

*One-time measurement taken in 1972.

Table B-4

PCBs Entering Lake Michigan From
Known Industrial and POTW Discharges*

State	PCB Load (lb/yr)	Source
Michigan	317.2	POTWs
Wisconsin	1170.1	Industries
Wisconsin	130.3	POTWs
Indiana	122.3	POTWs
Illinois	3.1	POTWs
Total	1643	

*See Tables B-5 - B-9 for tabulations of the individual waste discharges.

TABLE E-5

Concentration of PCBs in Treated Michigan WTP Effluents Tributary to Lake Michigan[1,2,3,4]

WTP Location	Design Flow (MGD, 1974)	[PCB] (ppb, '71-'72)	PCB Load (lb/day)
Albion	4.0	0.44	0.015
Battle Creek	22.0	0.39	0.017
Benton Harbor, St. Joseph Plant	13.0	0.65	0.070
Menominee	1.2	0.35	0.004
Muskegon	10.0	0.28	0.023
Niles	10.0	0.68	0.056
Portage	3.6	1.9	0.057
East Lansing	6.5	0.5	0.035
Kewaunee	2.2	0.29	0.005
Holland	4.5	0.6	0.022
Jackson	20.0	<0.1	
Kalamazoo	14.0	0.66	0.106
Lansing	34.0	0.18	0.051
Total	147.0*		0.595*

PCB Load = 0.595 lb/day = 217.2 lb/yr.

* Total does not include flows with [PCB] <0.1 ppb.

TABLE E- 6

Concentration of PCBs in Reported Wisconsin Paper Plant Effluents Discharging to Green Bay (12/4-7?) (5)

Plant	Flow (mgd)	[PCB] (µg/l)	PCB Load (lb/day)
Badger Paper Mills	4.79	<.1	-
Scott Paper			
Marinette	5.91	<.1	-
Oconto Falls	11.03	<.1	-
Shawano Paper	3.43	<.1	-
John Strange Paper	1.11	4.00	0.037
Menasha Paper	5.22	28.40	1.26
Kimberly Clark	4.30	0.28	0.010
Thilmany Paper	25.1	<.1	-
Fort Howard Paper			
Mill Effluent	7.3	2.60	0.158
Deinking	11.04	6.40	0.586
Deinking & Mill Effluent	18.1	7.07	1.06
American Can			
Sulfite Sewer	2.33	0.1	0.002
Paper Mill Lagoon	10.35	0.14	0.012
Charmin Paper	16.3	0.14	0.019
Green Bay Packaging	1.77	0.45	0.006
Total*	77.65		3.15

PCB load = 3.15 lb/day = 1,150 lb/yr.

* Total does not include flows with [PCB] <0.1 ppb.

TABLE E-7

Concentration of PCBs in Selected Wisconsin Miscellaneous Industrial Effluents Discharged to Lake Michigan (5)

Plant	Flow (mgd)	[PCB] (ppb)	PCB Load (lb/day)
Motor Casting Co.	0.22	<0.1	
Osey Iron Foundry, Inc.	0.339	<0.2	
Bennett, Corp. - Crucible Steel	0.796	<0.1	
Maynard Steel Casting Corp.	0.133	<0.1	
Milwaukee Solvay Coke Co.	4.3	<0.1	
Briggs & Stratton	1.523	<0.2	
Weir Steel Co.	0.228	<0.1	
EPP Co.	0.069	3.95	0.001
Milwaukee Die Casting Co.	0.012*	32.2	0.003
Meta-Mold Eaton Malleable Inc.	0.033*	170.3	0.047
Babcock & Wilcox Co. Tubular Products Div.	0.6	0.9	0.004
Total**	0.714		0.055

PCB load = 0.055 lb/day = 20.1 lb/yr.

* Average of two readings.

** Total does not include flows with [PCB]<0.1 ppb.

TABLE B-6

Concentration of PCBs in Imported Wisconsin WTP Effluents Discharged to Green Bay (1974-75) (5)

WTP location	Flow (mgd)	[PCB] (ppb)	PCB load (lb/day)
Marinette	2.5	<0.1	
Portage	0.736	5.0	0.031
Oshkosh	6.49	0.1	0.007
Neenah-Menash	12.75	0.16	0.017
Appleton	11.05	0.12	0.011
Kaukauna	1.25	<0.1	
DePere	23.45	0.5	0.01
Green Bay	30.64	<0.1	
Kewaunee	0.315	0.38	0.001
Two Rivers	2.28	0.2	0.004
Manitowoc	9.3	<0.1	
Sheboygan	11.04	1.1	0.11
Port Washington	1.59	0.2	0.003
Milwaukee (South Shore)	66.7	0.29	0.160
Milwaukee (S. Milwaukee)	2.42	0.13	0.003
Racine	16.92	<0.1	
Kenosha	10.88	<0.1	
Total	119.8*		0.357*

PCB load = 0.357 lb/day = 130.3 lb/yr.

* Total does not include flows with [PCB]<0.1 ppb.

TABLE B-9

Concentration of PCBs in Imported Indiana NPS Effluents Tributary to Lake Michigan(6)

NPS Location	Flow (mgd)	[PCB] (µg/L)	PCB Load (lb/day)
Michigan City	13.2	1.32	0.134
Valparaiso	4.0	0.24	0.008
Mishawaka	2.9	0.23	0.006
Hammond	42.6	<0.1	
East Chicago	18.7	0.1	0.016
Chesterton	1.6	<0.1	
Gary	50.5	0.38	0.159
Fourth Bend	35.8	<0.1	
Mishawaka	10.39	0.13	0.011
Elkhart	17.5	<0.1	
Goshen	4.8	<0.1	
Nappanee	0.9	<0.1	
Kendallville	1.2	<0.1	
La Grange	0.185	<0.1	
Ligonier	0.434	<0.1	
Angola	0.784	0.17	0.001
Syracuse	0.305	0.13	0.0001
Total*	99.8		0.135

PCB load = 0.135 lb/day = 122.3 lb/yr.

* Total does not include flows with [PCB] <0.1 µg/L.

TABLE E-10

Lake Michigan Basin Hydrology[7,8,9,10,11]

Total mean river discharge (1974) of the 4 states (Michigan, Illinois, Wisconsin, and Indiana) into Lake Michigan = 34,508 cfs
= 1.1×10^{12} cf/yr

Total flow of water in the basin = 9.4 billion gpd
Flow diverted from Lake to Chicago = 2 billion gpd
Flow diverted through Straits of Mackinac = 67,000 cfs
Other withdrawal's from the Lake = 11.7 mgd

Volume of STP effluents entering Lake:
From Illinois = 37.6 mgd
From Indiana = 110.5 mgd
From Michigan = 161.6 mgd
From Wisconsin = 183.4 mgd

TABLE B-11

Estimates of Fish Biomass in Lake Michigan (1972-73)[12]

Michigan Waters of Lake Michigan - 11.2×10^6 lb. of lake trout (age group II & older); 1972

Northern Lake Michigan - 55×10^6 lb. of whitefish (age groups I-VI); 1972

From bottom trawls of the Lake - 220×10^6 lb. of alewife (age groups I & over); 1973

- 15×10^6 lb. of chubs (age groups I & over); 1973

Total (1972-73) = 3×10^8 lb.

a. Lake trout (from Michigan waters of the lake) - 11.2×10^6 lb (1972)
b. Whitefish (in Northern Lake Michigan) - 55×10^6 lb (1972)
c. Chubs (those available to bottom trawls) - 15×10^6 lb (1973)
   (note: decline in chubs from 139×10^6 lb in 1963-65)
d. Alewives (those available to bottom trawls + estimate of the midwater individuals) - 2×10^8 lb (1973)
e. Coho Salmon (estimate based on the number stocked) - 7.6×10^5 lb (1972)
   Total = 3.1×10^8 lb (1972-73)

Estimates for the Plankton Biomass:

a. Assume 300 kg plankton/hectare of lake
b. Area of lake = 22,400 mi^2 = 5.8×10^7 hectares[13]
c. Plankton biomass = (5.8×10^7) (300 kg) = 1.74×10^{10} g = 3.8×10^7 lb

In addition, the relatively polluted nature of the southernmost portion of the lake results in large masses of benthic species, such as tubifex worms. In view of this, it is assumed that the benthic biomass is of the order of 4×10^7 lbs.

TABLE B-12 (14)

Representative PCB Measurement

Biota

a.	PCB in fish (alewives, smelt, slimy sculpin)	= 2.35 - 5.13 x 10^5 ppt
b.	PCB in water (total conc. dissolved + particulate)	= 55 ppt
c.	Average PCB in sediments	= 1.2 x 10^5 ppt
d.	Average PCB in wet plankton	= 7.2 x 10^5 ppt
e.	PCB in the benthos	= 4.7 x 10^5 ppt

APPENDIX B REFERENCES

1. Schacht, P.A.; Pesticides in the Illinois Waters of Lake Michigan, EPA 660/3-74-002, U.S. Environmental Protection Agency, Jan., 1974.

2. State of Michigan Water Resources Commission, Bureau of Water Management, Polychlorinated Biphenyl Survey of the Kalamazoo River and Portage Creek in the Vicinity of the City of Kalamazoo 1972.

3. Hesse, J.L.; Status Report on Polychlorinated Biphenyls in Michigan Waters. Report to Michigan Water Resources Commission, 1973.

4. State of Michigan Water Resources Commission, Bureau of Water Management, Monitoring for Polychlorinated Biphenyls in the Aquatic Environment. Report to Lake Michigan Toxic Substances Committee, May, 1973.

5. Kleinert, Stan; Chief of Water Quality Surveillance Section, DNR Wisconsin, Personal Communication, 1975.

6. Winters, John; Acting Chief of Water Quality and Standards Branch of Illinois EPA, Personal Communication, 1975.

7. United States Geological Survey, Water Resources Data for Michigan, Part 1. Surface Water Records, 1972.

8. United States Geological Survey, Water Resources Data for Wisconsin, Part 1. Surface Water Records, 1974.

9. United States Geological Survey, Water Resources Data for Illinois, Part 1. Surface Water Records, 1974.

10. United States Geological Survey, Water Resources Data for Indiana, Part 1. Surface Water Records, 1974.

11. Saylor, J.H., P.W. Sloss; Water Volume Transport and Oscillatory Current Flow through the Straits of Mackinac. (Contribution No. 38, Great Lakes Environmental Research Laboratory), 1957.

12. Michigan Department of Natural Resources Fisheries Division, Estimates of Biomass of Principal Fish Species in the Great Lakes (first report). Fisheries Research Report No. 1815, 1974.

13. The Lake Michigan Federation, "The Lake Michigan Basin", March, 1975.

14. National Water Quality Inventory, "Report to the Congress. Vol. II", EPA-440/9-74-001. USEPA, 1974

The literature resulting from analytical measurements on a wide variety of biological and geological specimens has become very large. The following list, while in no sense complete, represents those sources used in this work.

(1) Addison, R.F., R.G. Keer, J. Dale, and D.E. Sergeant, J. Fish Res. Board Can., 30, 595, 1973.

Anonymous, "Chemicals Found in Lake Fish: State PCB Ban Urged." Michigan Out-of-Doors, July, 1975.

Bailey, S., P.J. Duryan, and F.B. Fleiwick. Chemistry and Industry 22: 709, 1970.

Bowes, G.W. and C. Jonkel, in PCB in the Environment, Marcel Dekker Inc., New York, 1974.

Carey, A.E., G.B. Weirsma, H. Tai, and W.G. Mitchell. Pesticides Monitoring Journal 6 (4): 369-376, 1973.

Crump-Weirsma, H.J., H.R. Pelts, and M.L. Yates. Pesticides Monitoring Journal 8(3): 157-161, 1974.

Duguchi, M., Dee Pesticide in Environmental Chemistry and Toxicology, Proceedings of the International Symposium, Suzuka, Japan, 1973, Coulston, F., Korte, F., and Goto, M., Eds., International Academic Printing Co., Tokyo, Japan, 1973.

Duke, T.W., J.I. Lowe, and A.J. Wilson, Jr. Bulletin of Environmental Contamination and Toxicology; 5(2): 171-180, 1970.

Edwards, R. "Polychlorinated Biphenyls, Their Occurrence and Significance: A Review." Chemistry and Industry (No Volume) Issue 47: 1340-8 (21 November, 71), 1971.

Fog, M., and I. Kraul, Acta Vet. Scand., 14, 350, 1973.

Frank, R., K. Ronald, and H.E. Braun, J. Fish Res. Board Can., 30, 1053, 1973.

Glen, C.S., M.K. Wong, A.R. Hanks, and W.M. Barnett, Bull. Environ. Contam. Toxicol., 9, 376, 1973.

Greichus, Y.A., A. Greichus, and R.J. Emerick, Bull. Environ. Contam. Toxicol., 9, 321, 1973.

Gustafson, C.G., Environmental Science and Technology 4(10): 814-819, 1970.

Harvey, G.R., H.P. Miklas, V.T. Bowen, and W.G. Steinhauer. Journal of Marine Research 32(2): 103-118, 1974.

Hopkinson, P.B., Mar. Pollut. Bull., 4, 44, 1973.

Hidaka, H., T. Ose, and K. Fujiwara, Eisakuhin Eiseigaku Zasshi, 13, 523, 1972; C.A., 79, 028100, 1973.

Hinderkeith, E., Beitr. Ver. Hygiene, Boden-, Lufthyg., Berlin-Dahl, 17, 103, 1972.

Hsu, W., R.W. Risebrough, A. Soutar, and D.R. Young. Science 184 (4142).

Interdepartmental Task Force on PCBs. "Polychlorinated Biphenyls and the Environment." COM-72-10419. 1-192. National Technical Information Service, Springfield, Virginia (U.S. Dept. of Agriculture, Commerce, Health-Education and Welfare, EPA, and other agencies), 1972.

Lowe, G., J. Soutar, and B. Josefsson. Bulletin of Environmental Contamination and Toxicology 13(6): 656-661, 1975.

Law, L.M., and D.P. Quarlite. Pesticides Monitoring Journal 8(1): 33-36, 1974.

Martell, J.M., D. A. Rickert, and F.R. Siegel. Environmental Science and Technology, 9: 972-75, 1974.

Oloffs, P.C., L.J. Albright, and S.Y. Szeto. Canadian Journal of Microbiology 18(9): 1393-1398, 1972.

Oloffs, P.C., L.J. Albright, S.Y. Szeto, and J. Lau. Journal of Fisheries Research Board of Canada, 30(11): 1619-1623.

Panel on Hazardous Trace Substances. "Polychlorinated Biphenyls-Environmental Impact." Environmental Research 5(3): 249-362. 1972.

Peel, D.A., Nature, 254: 324-325, 1975.

Risebrough, R.W., P. Reiche, D.B. Peakall, S.G. Herman, and M.N. Kirven, Nature (12/14): 1098-1102, 1968.

Risebrough, R.W., and B. deLappe. Environmental Health Perspectives Exp 1: 39-45, 1972.

Sandhurdenker, P.W., Can. J. Comp. Med., 37, 203, 1973.

Smith, W.E., F. Fish, and M.E. Babih, J. Fish. Res. Board Can., 30, 702, 1973.

Walker, W.H., "Where Have All the Toxic Chemicals Gone?" Ground Water 11(2): 11-20, 1973.

(2) Anon., World Almanac, Washington Star News, Washington, D.C., 1975.

National Water Quality Inventory. Report to the Congress. Vol. II. EPA-440/9-74-001. Office of Water Planning and Standards. Appendices C-1 to C-69, D-1 to D-55, E-1 to E-76., 1974.

(3) Reverse, A., J.M. Ogata, and J.W. Hylin. Bulletin of Environmental Contamination and Toxicology 8(4): 238-241, 1972.

Risebrough, T.F., and C.E. Olney. Science 183 (4112): 516-518. 2nd Copy, 1974.

Bidleman, T.F., and C.E. Olney. Bulletin of Environmental Contamination and Toxicology 11(5): 442-450, 1974.

Harvey, G.R., and W.F. Steinhauer. Atmospheric Environment 8(8): 777-782, 1974.

Holden, A.V. Nature 228(12/19): 1220-1221, 1970.

Sidersyan, A. Nature 236: 395-397, 1972.

Tarrant, R.R., and J.O.G. Tatton. Nature 219: 725-727, 1968.

(4) Panel on Hazardous Trace Substances. Environ. Res., 9, 1972.

(5) Benyston, B.A., Ambio, 3 No. 3, p. 84, 1974.

(6) Ruttner, F., 1952, Fundamentals of Limnology, University of Toronto Press. 295 p., 1952.

(7) Murray, D., and A.W. Walkoff. Environmental Science and Technology 7(7): 611-614, 1973.

(8) Saylor, J.H., and P.M. Sloss. Water Volume Transport and Oscillatory Current Flow Through the Straits of Mackinac. (Contribution No. 18, Great Lakes Environmental Research Laboratory), 1975.

(9) State of Michigan Water Resources Commission, Bureau of Water Management. Polychlorinated Biphenyl Survey of the Kalamazoo River and Portage Creek in the Vicinity of the City of Kalamazoo, 1972.

State of Michigan Water Resources Commission, Bureau of Water Management. Monitoring for Polychlorinated Biphenyls in the Aquatic Environment. Report to Lake Michigan Toxic Substances Committee, May, 1973.

Haile, C.L., G.D. Veith, G.F. Lee, and W.C. Pyle, Chlorinated Hydrocarbons in the Lake Ontario Ecosystem, 1973.

(10) Follows from Mean Value Theorem; See for example, "Advanced Calculus," E.B. Dobelnikoff, Holden, 1939, pp. 113ff.

(11) U.S. Dept. Interior, Federal Water Pollution Control Administration, Water Pollution Problems of Lake Michigan and Its Tributaries, January 1968.

(12) Manly, Brock. Personal communication.

(13) Handbook of Physics, E.U. Condon & H. Odishaw, McGraw-Hill, New York, 1967, Section 5-11ff.

(14) Hiebert, Ian. Personal communication.

(15) American Physical Society Handbook, 2nd Edition; D.E. Gray, Ed., McGraw Hill, New York, 1963; Table 2r-3, pp. 2-208.

(16) Polk, R., D. Grimes and R. Hollenbeck, "Laboratory Study of the Release of Pesticide and PCB Materials to the Water Column During Dredging and Disposal Operations," under Contract DACW 39-74-C-0142, December 1975.

(17) See Reference (6).

(18) Assoc., World Almanac, Washington Star News, Washington, D.C., 1975.

National Water Quality Inventory, Report to the Congress, Vol II, EPA-440/9-74-001, Office of Water Planning and Standards, Appendices C-1 to C-69, D-1 to D-55, E-1 to E-76, 1974.

Great Lakes Basin Framework Study, Great Lakes Basin Commission, April 11, 1975.

(19) (a) Dept. of the Interior and New York Dept. of Health, "Water Pollution Problems and Improvement Needs - Lake Ontario and St. Lawrence River Basins," June, 1968.

(b) Great Lakes Water Quality Board, "Great Lakes Water Quality, 1973 Annual Report to the International Commission," April, 1974.

(c) International Lake Erie Water Pollution Board, and the International Lake Ontario-St. Lawrence River Water Pollution Board, "Pollution of Lake Erie, Lake Ontario and the International Section of the St. Lawrence River," Vol. 1, 2, 3 (1969).

(d) U.S. Dept. of Interior, Federal Water Pollution Control Admin., "Water Pollution Problems of Lake Michigan and Tributaries," January, 1968.

(e) Sly, P.G. J. Fish. Res. Bd. Can., 33, pp. 135-169, 1976.

(f) Kemp, A., T.R. Dell & J. Jagnet. J. Fish. Res. Bd. Can., 33, 440-462, 1976.

(g) Greenmil, R. & A. Napier, "Standard Encyclopedia of World's Rivers and Lakes," Putnam, New York, 1965.

(h) Kemp, A.L., T.W. Anderson, R.C. Thomas and A. Mahadevan. J. of Sedimentary Petrology, 44, 207-218 (1972).

(20) Hague, R., D.H. Ostwalding, and V.W. Freed. Environmental Science and Technology 8(2): 139-142, 1974.

(21) "Background to the Regulation of PCBs in Canada," Environmental Contaminants Committee of Canada, April 1, 1976. Tech. Report 76-1.

(22) Monsanto, Tech. Bull. O/PL-106A.

(23) Obtained from integration of the Clausius - Clapeyron equation assuming that the heat of vaporization is constant. See, for example, "Physical Chemistry," S. Glasstone, Van Nostrand, New York, 1946, pp. 1xxff.

(24) Hutzinger, O., S. Safe, and V. Zitko. "The Chemistry of PCBs." CRC Press, Cleveland, Ohio, 1974.

(25) Hutzinger, O., S. Safe, and V. Zitko. "The Chemistry of PCBs." CRC Press, Cleveland, Ohio, 1974.

(26) Hayes, R., and C.W. Schwemberg. Bulletin of Environmental Contamination and Toxicology 14: 13-18, 1975.

(27) Kennard, E.H. "Kinetic Theory of Gases," McGraw-Hill, N.Y., 1938.

(28) Langmuir, "Phenomena, Atoms and Molecules," Philosophical Library, N.Y. Chapt. 15, 1950.

(29) Handbook of Physics, E.U. Condon & H. Odishaw, McGraw-Hill, New York, 1967. Section 5-15ff.

(30) American Physical Society Handbook, 2nd Edition, D.E. Gray, Ed., McGraw-Hill, New York, 1963, Table 2c-3, pp. 3-208.

(31) Parker, R. and I. Bersen. Biosciences, No. 87 (1970).

(32) Hutzinger, O., S. Safe, and V. Zitko. "The Chemistry of PCBs." CRC Press, Cleveland, Ohio, 1974.

(33) Biddleman, T.F., and C.E. Olney. Bulletin of Environmental Contamination and Toxicology 11(5): 442-450, 1974.

(34) Sandler, M.E. & Ha Shik Jhun. Ann. Rev. Phys. Chem., 17,373 (1969).

(35) Branson, D.R., Blau, G.E., Alexander, H.C., and Neely, W.B. "Bioconcentration of 2,2'4,4'-Tetrachlorobiphenyl in Rainbow Trout as Measured by an Accelerated Test," Trans. American Fisheries Society, CIV (1975), pp. 785-792.

(36) Williford, Wayne A., Hesselberg, Robert J., and Nicholson, Lawrence W. "Trends of Polychlorinated Biphenyls in Three Lake Michigan Fishes," Conference Proceedings - National Conference on Polychlorinated Biphenyls (NOV. 19-21, 1975), Washington, D.C.: EPA, March 1976.

(37) Hansen, D.J., Parrish, P.R., Lowe, J.I., Wilson, A.J. Jr., and Wilson, P.D. "Chronic Toxicity, Uptake, and Retention of Aroclor(R) 1254 in Two Estuarine Fishes," Bulletin of Environmental Contamination and Toxicology, VI (1971), pp. 113-119.

Neely, W. Brook. A Material Balance Study of Polychlorinated Biphenyls in Lake Michigan. Midland, Michigan: Environmental Sciences Research, The Dow Chemical Co.

(38) Vaith, G.D. Transcriptions of Hearings, Wisconsin Dept. Natural Resources, Madison, Wisc., August 28, 1975.

(39) Versar, Inc., PCBs in the United States: Industrial Use and Environmental Distribution, NTIS PB-252 402/AS, February 1976, Appendix D.